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PESTICIDES RESEARCH AND MONITORING ANNUAL REPORT (1986-1987)

Environment Canada

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EXECUTIVE SUMMARY

This is the first Annual Report on the Pesticides Program of Environment Canada. It summarizes the research and monitoring activities being conducted in all areas of the country by various sectors of the department.

The projects carried out under the program are listed in this report according to the region in which the field work was done.

Studies in the Pacific and Yukon region addressed two major areas of concern; the impact of herbicides on fisheries, and the presence of chlorophenols in the environment. Herbicides such as 2,4-D and Roundup are used in forestry and chlorophenols are used as wood preservatives at saw mills and lumber export terminals.

In the Western and Northern region, the studies addressed the impact of pesticides (in general); the effects of grasshopper insecticides on bird populations; and the effects of the run-off of pesticides from agricultural land to surrounding water bodies. Major watersheds studied included the North Saskatchewan, the South Saskatchewan, and the La Salle.

In the Ontario region, most of the studies were done to identify more sensitive techniques which could be used for monitoring pesticides in the environment. Some of these techniques included the use of sensitive animal species and plankton to detect the presence of low pesticide levels. The other major area studied in this region was off-target drift of pesticides from aerial spraying.

In Quebec, most of the studies were on the development of more sensitive biological methods to monitor the effects of pesticides on birds. Also, a study was done to determine the pesticide use pattern around residences in the Lakeshore area of Quebec.

In Atlantic Canada, the Pesticides Program concentrated on the presence and impact of budworm insecticides on fish and of forestry herbicides on vegetation, the presence of aldicarb in groundwater in Prince Edward Island, and the distribution of antifouling chemicals in the region.

Readers are encouraged to peruse the articles pertaining to their areas of interest and to contact the individual listed at the end of each article for more information. An index containing an alphabetical listing of the pesticide active ingredients is provided at the end of the report to assist readers in identifying all studies done on a particular chemical.

PESTICIDES PROGRAM IN THE PACIFIC AND YUKON REGION

(British Columbia and Yukon Territory)

1. TOXICITY OF SELECTED FORMULATIONS OF 2,4-D AND 2,4-D/DIESEL OIL MIXTURES TO RAINBOW TROUT (M.T. Wan)

Introduction:

2,4-D is a post-emergent herbicide used for the selective control of broad-leaved vegetation in agriculture, forestry, and on rights-of-way. In the coastal forest areas of British Columbia, 2,4-D is used in conifer release, logging road rights-of-way, and forest rehabilitation programs for the control of broad-leaved plants such as: alder, maple, birch, and other species.

In British Columbia, the most commonly used formulations in forestry are: 2,4-D dimethylamine (DMA), 2,4-D diethanolamine (DEA), and 2,4-D iso-octyl ester (IOE). Sometimes these formulations are mixed with various concentrations (volume/volume) of diesel oil, particularly the IOE formulation, in order to enhance adherence and absorption. Until the present investigation, little data were available on the toxicity of different formulations of 2,4-D in mixtures of diesel oil to fish. Typically, 2,4-D and water (85 to 90%) are mixed with diesel oil (10 to 15%) in actual spray mixtures. However, there were concerns about the toxicity of such herbicide/oil mixtures to salmonid fish species.

During 1983/1984 at the request of the British Columbia Fisheries Branch, and to assist the regional office of the Environmental Protection Service (EPS) in the evaluation of provincial permit applications for aerial and ground-based use of 2,4-D in oil mixtures, static fish bioassays were conducted to determine the toxicity of these herbicide/oil mixtures to fish.

Methodology:

In 1983/1984 static fish bioassays on rainbow trout were conducted by EPS, Pacific Region, to compare the acute toxicity of various formulations of 2,4-D and their mixture with different concentrations of diesel oil.

Results and Discussion:

2,4-D (DMA) was the most toxic formulation to rainbow trout (96-h LC_{50} = 58.6 mg/L); followed by 2,4-D (IOE) (96-h LC_{50} = 70.3 mg/L); and 2,4-D (DEA) (96-h LC_{50} = 314.9 mg/L). The addition of 5% diesel oil to the 2,4-D formulations increased the toxicity to rainbow trout by 3.2 times for 2,4-D (DEA); 1.7 times for 2,4-D (DMA); and 2.6 times for 2,4-D (IOE).

Conclusions:

1. The toxicity of 2,4-D to rainbow trout varies with the type of formulation.
2. The addition of 5% diesel oil (by volume) to the herbicide/water mixtures increases the toxicity to rainbow trout of the DEA, the DMA, and the IOE formulations of 2,4-D by 3.2, 1.7 and 2.6 times, respectively.
3. The toxicity to rainbow trout of 2,4-D IOE increases with increasing concentrations of diesel oil. No further increase in toxicity to rainbow trout results from increasing the oil concentration by greater than 25%.

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2. TOXICITY OF THE HERBICIDE GLYPHOSATE (ROUNDUP) AND ITS SURFACTANT TO SALMONIDS (M.T. Wan et al.)

Introduction:

Roundup is the trade name of a formulated herbicide containing the active ingredient glyphosate. It is used as a selective or non-selective post emergent treatment to remove unwanted vegetation in agriculture, forestry, and rights-of-way. In the coastal forest areas of British Columbia, glyphosate has the potential to replace the phenoxy herbicides, such as 2,4-D, for brown/burn and conifer release programs.

The objective of this study was to assist the EPS regional office in the evaluation of provincial permit referrals for aerial and ground-based spray applications of Roundup. A fish bioassay program was initiated in 1980 to determine the acute toxicity of Roundup and its surfactant to juvenile Pacific salmon.

Methodology:

In 1984, static fish bioassays were conducted by EPS, Pacific Region, to determine the acute toxicity of the herbicide "Roundup" and its surfactant "MONO-818" to juvenile salmonids.

Results and Discussion:

This study indicated that Roundup was moderately toxic to two species of Pacific salmon. The average 96-h LC_{50} value for: Coho salmon was 42.3 mg/L and 32.4 mg/L for Rainbow trout. The surfactant MONO-818 was highly toxic to salmonids, with 96-h LC_{50} values of 3.2 mg/L and 3.5 mg/L for Rainbow trout and Coho salmon, respectively. The stabilization time of LC_{50} values varied with different fish for Roundup, but appeared to be 96 hours for surfactant MONO-818. Analytical results of selected test water samples indicated that the free acid equivalent of glyphosate in Roundup was approximately 30%. Also glyphosate did not degrade to any significant degree during the 96-hour test period.

Conclusions:

1. Roundup is moderately toxic to juvenile Pacific salmonids (Coho and Rainbow trout) with an average 96-h LC_{50} value of 34.9 mg/L (range, 26.7 to 42.3 mg/L).

2. Roundup surfactant MONO-818 is about ten times more toxic (than Roundup) to juvenile Pacific salmonids (Coho salmon and Rainbow trout) with an average 96-h LC_{50} value of 3.4 mg/L (range, 3.2 to 3.7 mg/L).

3. Low concentrations of glyphosate (i.e., 0.025 to 0.100 mg/L) in stream water is unlikely to have any short-term impact on fish.

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3. ACUTE TOXICITY OF GARLON 3A, GARLON 4, TRICLOPYR, TRICLOPYR ESTER AND THEIR TRANSFORMATION PRODUCTS TO JUVENILE PACIFIC SALMONIDS (M.T. Wan et al.)

Introduction:

Garlon 3A and Garlon 4 are formulated triclopyr herbicides manufactured by The Dow Chemical Company. These products are selective post-emergent herbicides used for the control of broad-leaved vegetation. Although not presently registered in Canada for forestry use, they have the potential to offer an additional choice of chemicals for conifer release programs in coastal British Columbia. The use of Garlon herbicides in such areas, however, could result in the unintentional introduction of triclopyr and its degradation products into waterbodies inhabited by salmonids.

The objective of this study was to evaluate the acute toxicity of formulated and technical triclopyr and its transformation products to juvenile salmonids of the Pacific Northwest.

Results and Discussion:

Garlon 3A, the amine product of triclopyr, is significantly less toxic to salmonids than Garlon 4, the ester formulation. Moreover, Garlon 3A and Garlon 4 are significantly less toxic to salmonids than their respective active ingredients triclopyr and triclopyr ester. This observation suggests that the emulsifiers used in formulating these products do not increase fish toxicity.

Triclopyr is significantly less toxic (eleven times less) to salmonids than triclopyr ester. Within species, triclopyr is more toxic to chum, sockeye salmon and rainbow trout than to coho and chinook. Triclopyr ester is more toxic to juvenile chum and sockeye salmon than to coho, chinook salmon and rainbow trout. The 96-h LC_{50} for Coho salmon exposed to triclopyr ester is 1.0 mg/L, confirming a recent study which reported this material to be highly toxic to both the juvenile and alevin stages of coho salmon. The respective 96-h LC_{50} values were 1.3 mg/L and 0.3 mg/L.

Test results for the two principal transformation products of triclopyr suggest that the pyridinol metabolite is somewhat more toxic to juvenile salmon than the pyridine. The pyridinol degradation product is also as toxic to young salmon as the formulated triclopyr ester. This transformation product is equally toxic to all species of juvenile salmon. The pyridine, however, is more toxic to pink salmon than to the other five salmonid species (coho, chum, chinook, sockeye and rainbow trout).

Conclusions:

This bioassay study indicates that Garlon 4, the ester formulation of triclopyr, is highly toxic to salmonids of the Pacific Northwest. In contrast, Garlon 3A, the amine formulation is considerably less toxic to fish. Of the two principal degradation products, the pyridinol metabolite is as toxic as Garlon 4 to juvenile salmonids, while pyridine seems to be more toxic to young pink salmon than the other salmon species tested. Indirectly, this study also suggests that the emulsifiers used for the formulation of Garlon 3A and Garlon 4 do not increase fish toxicity.

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4. THE PERSISTENCE OF GLYPHOSATE AND ITS METABOLITE AMINO-METHYL-PHOSPHONIC ACID (AMPA) IN SOME BRITISH COLUMBIA COASTAL STREAMS (M.T. Wan)

Introduction:

Glyphosate (Roundup) is used in agriculture and forestry as a selective or a non-selective post-emergent herbicide to remove unwanted vegetation. In the coastal forest areas of British Columbia, it has the potential to replace the phenoxy herbicides such as 2,4-D for brown/burn and conifer release programs.

Prior to this study, there were no data available on the environmental behaviour of glyphosate under local conditions. Information was required on the potential impact of glyphosate on the west coast fishery if this herbicide is used extensively in forestry. To assist the EPS regional office in the evaluation of provincial permit applications for aerial and ground-based use of glyphosate, a monitoring program was initiated in 1981 to assess the persistence of glyphosate and its metabolite amino-methyl-phosphonic acid (AMPA) in British Columbia coastal streams.

The monitoring objectives were: 1). to determine the levels and persistence of glyphosate and AMPA in water and sediments of streams protected and not protected by buffer zones during aerial and ground-based spray operations; 2). to establish the concentration, if any, of these chemicals in a creek when a large area of its watershed was aerially treated with Roundup; and 3). to determine the sediment/water partitioning properties of glyphosate and AMPA.

Methodology:

From 1982 to 1984, EPS, Pacific Region, conducted studies at the University of British Columbia Research Forest and Chilliwack/Sechelt forest districts to monitor the residues of glyphosate and its metabolite, AMPA, in stream water and sediment. The objective of these studies was to evaluate the persistence of these chemicals in coastal streams protected and unprotected by a buffer zone during aerial- and ground-based operational sprays.

Results and Discussion

Glyphosate residues in unprotected stream water reached 0.023 mg/L within 2 to 3 hours following aerial application of active ingredients at 3 kg/ha. Residues peaked at 0.100 mg/L following the first major rainstorm eight days later, then dropped to levels below the detection limits of 0.005 mg/L within two weeks. In two protected streams, the highest water level detected was 0.025 mg/L, following several heavy rainstorms. In both the protected and unprotected streams, the concentration of AMPA in water was below the detection limit (0.005 mg/L) during the study period.

One week after spray application, glyphosate residue in a sediment sample from the unprotected stream was 0.100 mg/kg. Peak levels of 0.400 mg/kg were detected at three weeks and three months post-spray; thereafter concentrations declined to 0.040 mg/kg which persisted for 574 days post-spray. AMPA residues were also found in the sediments, peaking at 0.400 mg/kg three months after treatment. This metabolite showed a more gradual decline to 0.090 mg/kg which also persisted for the study duration (574 days).

Glyphosate residue in a sediment sample from a protected stream was 0.200 mg/kg one week after an aerial spray application 3 kg/ha. Herbicide residues from vegetation along the stream bank or in the treated area may have washed into the creek following major rain events. AMPA residues (0.100 mg/kg) were detected only once in this stream, 15 days after treatment. Both glyphosate and AMPA residues were below the detection level in protected stream sediments for the remainder of the study (600 days post-spray).

Conclusions:

1. Glyphosate was detected in water immediately after aerial treatment in a creek that was not protected by a buffer zone, despite good stream bank vegetation cover, but not in two creeks protected by buffer zones.
2. Glyphosate and AMPA were detected in the sediment of the unprotected (treated) creek after the first rainstorm; residues persisted for the duration of the study (574 days).
3. Very low concentrations of glyphosate and AMPA were found briefly in the water and sediment of one of the protected creeks. The entry of the chemicals into the watercourse was attributed to the frequency and intensity of rainstorms which carried glyphosate-contaminated soil particles into the stream.
4. Laboratory and field observations indicated that glyphosate adsorbed onto sediment particles was not readily released to the water phase.

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5. THE PERSISTENCE OF TRICLOPYR AND ITS PYRIDINOL METABOLITE IN A BRITISH COLUMBIA COASTAL STREAM (M.T. Wan)

Introduction:

Triclopyr (Garlon) is a selective post-emergent herbicide used for the control of unwanted broad-leaved vegetation in agriculture and woody plants in forestry. In the coastal forest areas of British Columbia, it has the potential to replace the phenoxy herbicides 2,4-D for conifer release programs. However, Garlon is presently not registered for forestry use in Canada.

The objective of this study was to assist the EPS regional office in the evaluation of the potential impact of triclopyr on salmonids.

Methodology:

In 1984, a monitoring study was conducted by EPS, Pacific Region, to determine the persistence of triclopyr and its pyridinol metabolite in stream water and sediment of British Columbia coastal areas.

Results and Discussion:

Triclopyr residues in stream water reached a level of 0.620 mg/L within 0.5 hours following an aerial overspray application of active ingredient at 0.91 kg/ha. These residues rapidly declined to 0.006 mg/L within one day, but low concentrations (0.001 to 0.003 mg/L) of triclopyr were detected for two months following the spray. The pyridinol metabolite was detected in stream water two days post-spray at 0.070 mg/L, and thereafter at 0.030 to 0.060 mg/L for two months following the spray application.

Both triclopyr and its pyridinol metabolite appeared in stream sediment at 0.14 mg/kg and 0.20 mg/kg respectively, four hours post-spray. Triclopyr and the pyridinol metabolite were also detected at low concentrations (0.02 mg/kg to 0.12 mg/kg) in sediment during the four months after the spray. After this period, these residues were not detected above the limit of detection in the sediment (i.e., 0.02 mg/kg).

Conclusions:

1. Triclopyr and its pyridinol metabolite can persist in very low concentrations (i.e., 0.001 to 0.006 mg/L) in flowing stream water for at least two months after a direct aerial overspray.

2. These chemicals do not seem to persist for more than four months in stream sediment at levels greater than 0.02 mg/kg under similar treatment conditions.

3. The degradation of triclopyr and its pyridinol metabolite in stream water and sediment is presently not well understood. More studies are required to better understand the degradation processes for these chemicals in the aquatic environment.

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6. PATHWAYS OF CHLOROPHENOLS IN THE FRASER RIVER ESTUARY (J.H. Carey and D.C.L. Lam)

Introduction:

The largest use of chlorophenols in Canada is for wood preservation where pentachlorophenol and tetrachlorophenol are used extensively. After conducting an extensive survey of the Great Lakes basin in which 77 out of 85 samples contained pentachlorophenol, National Water Research Institute (NWRI) scientists began studies on the aquatic pathways for accumulation and degradation of this nearly ubiquitous contaminant. Degradation rates and products of chlorophenols are dependent on the system under study. Attached biofilms in shallow rivers and streams are very efficient at degrading chlorophenols and half-lives are in the order of hours. In deeper, slower-mixing systems, photodegradation is most important and half-lives are measured in days or weeks. In soils and anoxic sediments, biological dechlorination reactions occur with half-lives of tens of years.

Bioaccumulation pathways were also studied and it was shown that many aquatic organisms accumulate elevated levels of chlorophenols by direct uptake from the water rather than via food chains. Canadian Wildlife Service researchers have found that herons and other birds in the Fraser River estuary contained elevated levels of dioxins. All higher chlorinated chlorophenol preparations contain chlorinated dioxins and furans as manufacturing impurities. Dioxins can also form in the low temperature combustion of chlorophenol-treated materials; however, the most toxic form of chlorinated dioxin (2,3,7,8-tetrachloro-) is not found in the chlorophenols used in the lumber industry. Since the discovery that birds in the Fraser River estuary had elevated levels of dioxins, NWRI's research has focussed on that system.

The objectives of this study were: 1). to determine the factors controlling bioaccumulation, transport and degradation of chlorophenols in the Fraser River estuary and to produce a contaminant transport and fate model for the estuary; and 2). to formulate a site-specific contaminants list for the estuary for use by the agencies designing the water quality plan under the Fraser River Estuary Management Program (FREMP).

Methodology:

Activities in support of the objectives will centre on sampling and analysis of river water, suspended solids, sediments and aquatic biota. Samples will be extracted, derivatized with acetic anhydride and analysed for chlorophenols by capillary gas chromatography with electron capture detectors. The chlorophenol isomer distribution in water, suspended solids and sediments will be determined and used to identify the factors controlling physical state and movement of these compounds. Biomagnification factors will be determined by comparing concentrations in biota with those in water.

Concurrent with sampling for chlorophenol distribution, measurements of temperature, conductivity, light transmission and water movement (from drogue studies) will be made. The data will be combined with existing physical simulation models to develop contaminant transport models for chlorophenols in the estuary.

Fish and sediment in the estuary will be analysed by capillary Gas Chromatography and Gas Chromatography/Mass Spectrometry (GC/MS) to determine the identities of major contaminants. Initial emphasis will be on saturated hydrocarbons, polycyclic aromatic hydrocarbons and organochlorine contaminants.

Results and Discussion:

Initial sampling concentrated on the North Arm of the estuary. Chlorophenols were observed at analytically significant levels in all fish and water samples. Pentachlorophenol and 2,3,4,6-tetrachlorophenol were the most prominent congeners. The geographical distributions and isomer ratios indicated that sawmills using chlorophenols for wood protection were the major sources. Concentrations in fish were 100 to 1400 times greater than those in water depending on species. There was disagreement between bioconcentration factors determined in this study and some published data from other countries. In addition, lower chlorinated congeners were present in some of the larger fish. The presence of these isomers is unexplained at this time. This information has been of interest to the Water Quality Branch (WQB) who are involved in a multi-agency effort to develop a water quality plan for the estuary under FREMP. NWRI scientists are currently involved with the WQB in analysing starry flounders from the system to evaluate their usefulness as a biomonitor.

During the year, two trips to the estuary were made to collect samples and data as part of an investigation into the transport dynamics of chlorophenols in this system under high and low flow conditions. Under high flow conditions, water velocities of several knots were observed and the residence times of a "plug" of water in the lower estuary, as measured with drogue markers, varied from three hours in the Main Arm to approximately ten hours in the North Arm. Salt water intrusion into the estuary was minimal and turbidities were high. Under these conditions, chlorophenol inputs would be carried out into the Strait of Georgia with little degradation or deposition. Under low flow conditions, water velocities were substantially reduced and residence times in the lower estuary were of the order of days. Under these conditions, some photodegradation can occur at the surface but overall residence times are still too low for substantial degradation to occur. Most of the chlorophenolic inputs, therefore, are carried out of the estuary and the fate of these compounds is ultimately determined by factors in the Strait. In collaboration with scientists at the Institute of Ocean Sciences, Department of Fisheries and Oceans (DFO), a computer model of the Fraser River plume in the Strait was modified and used to predict the extent and direction of the plume during sampling trips. The model predictions for low flow conditions were qualitatively confirmed by observation.

A survey was conducted to identify the major contaminants in fish from the estuary. These were: p,p'-DDE, alpha-chlordane, penta- and tetrachloroanisoles, hexachlorobenzene and a number of chlorinated biphenyl isomers. The chlorobiphenyl isomer pattern indicated sources of Aroclor 1260 in both Arms and a source of Aroclor 1254 in the North Arm. Further analyses are underway.

Suspended sediment was sampled with a portable centrifuge and analysed for a variety of contaminants. Contaminant levels were low; many compounds, including chlorophenols, were not detected. Since partitioning of organic contaminants to the sediment depends on carbon content, which in this case was only about 3%, this result is readily explained. These observations lead to the conclusion that unless the contaminant enters the system already adsorbed on a highly organic sediment (e.g., sewage sludge), sediment partitioning within the estuary will be unimportant and transport to the Strait of Georgia will occur primarily in the water phase.

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7. CHLOROPHENOL CONTAMINATION OF STORMWATER DISCHARGES AT SELECTED FRASER RIVER SAWMILLS (P. Krahn)

Introduction:

Approximately 32% of the world's softwood lumber is exported annually from British Columbia. Much of this lumber, especially overseas shipments, must be protected against sapstain and mold attack. Freshly cut lumber is typically treated with a surface application of a 1 to 2% chlorophenate solution. The chlorophenates are formulated as water-soluble sodium salts and are applied to the lumber by either dip or spray application at sawmill and lumber export operations.

Chlorophenate solutions may enter the environment from the sites of chemical storage and application, lumber drip areas and final-treated lumber and storage yards. Environment Canada and the B.C. Ministry of Environment and Parks are currently implementing a code of practice to contain chlorophenate releases at sawmill and lumber export operations. Many remedial measures have occurred during mill modernization. However, the forest products industry has not prevented or contained chlorophenate releases from final-treated lumber storage sites. Most treated lumber is stored uncovered in storage yards. Chlorophenate residues are either leached or washed off lumber during rainstorm events and contaminated water enters storm drains discharging to the Fraser River and other bodies of water.

Methodology:

A monitoring program was initiated in August 1986 to better define and quantify stormwater discharges from lumber storage yards at five sawmills on the lower Fraser River and at two lumber export terminals in North Vancouver. Catchment basins in lumber storage yards were isolated and sampled at the manhole prior to stormwater discharge to sewer. Manual grab samples of chlorophenate-contaminated stormwater were collected in one-litre amber glass bottles and combined as composite samples. Approximately three storm events were monitored at quality parameters and flow were also determined on each sampling occasion.

Results and Discussion:

1. Lumber treated by dipping will leach at an average of 52 000 ppb total chlorophenates (CPs). The concentrations experienced at the storm drain were found to average 430 ppb total CP.

2. Lumber treated by low pressure spray and subjected to rainfall with little or no drying time will produce grossly contaminated runoff which averages 30 000 ppb total CP or higher.

3. Lumber treated by low pressure spray and allowed eight days of drying time will leach up to 8000 ppb total CP. The concentrations experienced at the storm drain were found to average 700 ppb total CPs or higher.

4. Lumber treated by high pressure spray and subjected to rainfall after several days drying time will produce leachate at 1000 ppb total CPs. The concentrations experienced at the storm drain were found to average 1000 ppb total CPs or higher.

Remedial measures to prevent stormwater contamination with chlorophenols are presently under investigation.

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8. PERSISTENCE OF DINOSEB AND ENDOSULFAN IN WATER AND SEDIMENTS ADJACENT TO PESTICIDE-TREATED FARMLAND

(M.T. Wan)

Introduction:

Farm A, located 32 km south of Vancouver, was selected for an investigation on the occurrence of dinoseb and endosulfan in the Fraser estuary.

Methodology:

The Dinoseb study was conducted in a ditch adjacent to a crop of peas. This herbicide was used as a post-emergence top killer. It was applied by means of a tractor-mounted boom sprayer in mid-June 1986. The rate of application of active ingredient was 5 L/ha.

Sediment and water samples were taken at random from the ditch. Five samples of each medium were taken during each sampling occasion. Sampling was conducted before dinoseb treatment and post-treatment following two major rainstorms. However, it was not possible to be present during the treatment day. Consequently, the 0.5-hour post-treatment samples were not taken.

The Endosulfan study was undertaken in another part of Farm A where a crop of potatoes was planted. This insecticide was used for the control of aphids and other insect pests. It was also applied by means of a tractor-mounted boom sprayer. The crop was treated on July 24, 1986 and the rate of application of active ingredient was 0.568 kg/ha.

Sediment and water samples were taken from an adjacent ditch. Top 5-cm soil samples were also taken from the tilled areas. Drift samples were collected during the time of the spray application by using petri dishes (~130 mm dia.).

Results and Discussion:

Dinoseb residues were not detected in water and sediment samples before the spray application. However, low levels of this herbicide were found in the water but not in the sediment following the first major rainstorm in early fall (mean conc. 0.004 ppm). Dinoseb residues were not detected following the second major rainstorm in December, 1986.

Endosulfan residues were detected on the drift plates placed at various distances from the treatment area. The amount deposited at 0 m, 2 m, and 3 m from the crop was equivalent to 246.9, 1.3 and 0.5 g endosulfan/ha, respectively.

Endosulfan residues were carried over in the top soil (5 cm) of tilled area of Farm A and in the adjacent ditch sediments. The concentration in the top soil was 0.219 ppm; the level in the ditch sediments was about 20 times lower (i.e., 0.011 ppm).

Shortly after treatment (i.e., 0.5 hour), endosulfan residues in the top 5-cm of soil increased to 1.712 ppm within the crop area. Residues then decreased to 0.674 ppm 60 days post-spray, and finally to 0.073 ppm another 80 days later.

In contrast, the top soil (5 cm) two metres outside the treated area contained 0.313 ppm soon after treatment (i.e., 0.5 hour). This level decreased to 0.164 ppm 60 days later and to 0.50 ppm 140 days later.

In the ditch sediments, the pre-spray level of endosulfan carried over from previous years was low (about 0.011 ppm). This level increased towards the fall and winter months following seasonal rainstorms. It increased from 0.003 ppm half hour post-spray to 0.012 ppm 60 days later and 0.054 ppm, 140 days later.

Endosulfan residues were not detected in the ditch water before treatment but the water contained 1300 ppb half an hour after the potato crop was treated with the insecticide. However, this insecticide was not detected in the ditch water 60 days and 140 days post-treatment.

Conclusions:

Although low levels of dinoseb were detected in the ditch water following the first major rainstorm, the results suggest that the herbicide was not carried over in the aquatic environment from year to year, at least not in the vicinity of Farm A.

In contrast, this survey suggests that endosulfan is not only carried over in the top soil of the crop area but also in the adjacent aquatic environment. The impact of sublethal concentrations of endosulfan in the 200 ppb range to soil dwelling organisms is not well known. However, the 11 ppb level in the ditch sediment is considered conducive to bio-accumulation in sediment-dwelling aquatic invertebrates and other organisms in the food chain.

While the amount of drift entering the adjacent ditch 2 m away from the treated area is estimated to be only about 0.09% of the total applied to the crop, it is sufficient to generate a level of 1300 ppb total Endosulfan I and II in the water soon after the spray application. This concentration in water exceeds the 96-h LC_{50} values of most aquatic invertebrates and fish by more than 200 times for Endosulfan I and 900 times for Endosulfan II.

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PESTICIDES PROGRAM IN THE WESTERN AND NORTHERN REGION

(Alberta, Saskatchewan, Manitoba, Northwest Territories)

1. PERSISTENCE OF INGESTED INSECTICIDES IN GRASSHOPPERS

(N.D. Wescott and A.B. Ewan, Toxicology Research Group, University of Saskatchewan, Saskatoon)

Introduction:

Much concern over the effects of widespread grasshopper spraying has been raised during the last four years by many public environmental groups and environmental agencies operating in the prairies. This study attempted to answer the question of how much insecticide is ingested by a grasshopper and how much of it remains in the grasshopper after a short period of time (24 hours). The ultimate purpose of this work was to establish the potential for secondary poisoning of non-target animals that are likely to eat poisoned grasshoppers.

The objectives of the study were:

1. to determine the concentration of dimethoate and its metabolite, dimethoxon, in grasshoppers that have consumed dimethoate-treated bran bait and in grasshoppers that have been sprayed with dimethoate; and

2. to determine how dimethoate and dimethoxon degrade over 24 hours in poisoned grasshoppers.

Methodology:

Young grasshoppers from the Agriculture Canada Research Station in Saskatoon were fed bran bait treated with dimethoate and were sprayed with dimethoate to simulate common application procedures used in the prairies. After the insects died they were separated into groups and left for varying periods of time before they were frozen, so the degradation of dimethoate in dead grasshoppers could be determined. The insects were ground up so the insecticide could be extracted from their bodies for analysis.

Results and Discussion:

It was found that grasshoppers eating bran bait died much faster than those that were sprayed, showing that dimethoate is more effective if it is eaten. Dimethoxon is the actual poison, it is metabolized from dimethoate by the grasshoppers. The research found that dimethoate levels declined rapidly over the 24-hour period to levels 25% of the initial body concentration. Dimethoxon levels, however, did not decline very much over the 24-hour time period. Dimethoxon concentrations comprised 25 to 30% of the dimethoate concentrations.

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2. EFFECTS OF ROADSIDE APPLICATION OF CARBOFURAN ON NESTING BREWER'S BLACKBIRDS

(L.P. Horstman, PECAN Resources Inc., Edmonton, Alberta)

Introduction:

Preliminary investigations identified the possibility that some birds were being killed by carbofuran sprayed to control grasshoppers. This field experiment was set up to determine if Brewer's blackbirds deliberately sprayed with this insecticide were adversely effected either physically or behaviourally.

The objective of this study was to determine if the widespread application of carbofuran (Furadan) could be having serious effects on a roadside-nesting species such as Brewer's blackbirds.

Methodology:

For comparison, two areas were selected, one for treatment and one for non-treatment. Once nests were found close to roadsides, the nests in the treated area were sprayed with carbofuran. The nests were visited regularly to determine how the nestlings were growing or if any had died. A group of sprayed nestlings were collected and killed to determine if the chemical had been assimilated and if the birds' brain levels of cholinesterase were depressed by their exposure to carbofuran.

Results and Discussion:

It was found that nestlings either received or retained little of the carbofuran to which they were exposed and brain and plasma cholinesterase levels were not depressed. The highest residues were found in a young bird away from its nest. The nest environment may provide some protection for young birds against contacting the insecticide. No effects were seen with respect to nestling success. Carbofuran is toxic only if the animal eats, inhales or absorbs the chemical. Feathers may provide protection by preventing absorption. From this study it can be tentatively concluded that nesting Brewer's blackbirds are not at risk from roadside spraying with carbofuran.

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3. DO SOME INSECTICIDES *CURRENTLY USED* FOR GRASSHOPPER CONTROL REDUCE PRODUCTIVITY OF BURROWING OWLS?

(Paul C. James (Contractor), Museum of Natural History, Saskatchewan Culture and Recreation, Regina, Saskatchewan)

Introduction:

The burrowing owl has been designated as a threatened species in Canada by the Committee on the Status of Endangered Wildlife in Canada (COSEWIC). This species is predominantly a bird of the grasslands and its distribution is therefore very similar to that of grasshoppers and grain farms. It nests in the abandoned underground burrows created by ground squirrels and badgers. Saskatchewan may hold two-thirds of the Canadian population. Although a progressive decline in numbers has been described in recent decades, the causes remain to be determined. Insects, predominantly grasshoppers, comprise the bulk of its diet particularly during the chick-rearing period. The objectives of this study were:

1. to determine the frequency and nature of landowner-applied insecticide exposure to burrowing owls nesting in an area with an economically significant grasshopper infestation; and

2. to determine if these exposures have a detrimental effect on the reproductive success of this species.

Methodology:

In 1986, a total of 99 randomly chosen pairs of burrowing owls breeding in the Regina and Val Marie areas of Saskatchewan were monitored. The success and maximum number of young observed above ground at all burrows was determined. Insecticide application histories were obtained from the landowners and municipalities. A previous study determined that 60% of the flights from the nest burrow were within 50 metres and 90% were within 400 metres. Any spraying event that occurred within 400 metres of an active nest burrow was regarded as a potential exposure.

Results and Discussion:

Only 33 of the 99 nesting pairs located in the two study areas were not subjected to at least one spray event within 400 metres of their nest burrow. Thirty-nine percent of the burrows exposed were subjected to 3 to 8 events, and 70% of the exposures were within 50 metres of the nest burrow. Over 75% of the burrows were exposed at least once as a result of municipal spraying of roadsides. A total of six insecticides were applied within 400 metres of one or more nest burrows. Carbofuran (Furadan), carbaryl (Sevin), and chlorpyrifos (Lorsban) accounted for 35%, 35% and 15% of the applications, respectively. The other insecticides used were deltamethrin, malathion, and methamidophos.

One or more exposures to carbaryl within 50 or 400 metres of the nest burrow had little effect on productivity. In marked contrast, exposure to carbofuran within 50 metres of the nest burrow was associated with statistically significant reductions of 54% in the number of young per nest and 50% in the proportion of pairs that raised one or more young, relative to the 50 metre control. The productivity of pairs exposed to both carbofuran and carbaryl within 400 metres of the nest burrow was 35% lower than those exposed to carbaryl alone. A small colony of five nests which was directly oversprayed with carbofuran failed to produce any young and adult mortality was suspected. The reproductive success of a colony of 14 nests directly oversprayed with carbaryl was 30% lower than in a nearby nonsprayed colony.

This initial study showed that in areas/years of moderate to severe grasshopper infestation, burrowing owls nesting in Saskatchewan are frequently exposed to insecticidal agents; some of which have a greater impact on reproduction than others. The available evidence suggests that the effects observed with carbofuran are due to its marked toxicity to this species and do not result from food removal. Hazard increases with proximity of the application to the burrow.

The carbaryl and carbofuran findings suggest that the relative impact on reproduction success of burrowing owls reflects the acute toxicity of the principal insecticides available for grasshopper control as judged by their acute toxicity to mallard ducks. If so, then highly toxic agents such as carbofuran and chlorpyrifos should not be applied within 400 metres of active burrowing owl nests. Active burrowing owl nests should not be directly oversprayed with any insecticide. The relative toxicity to beneficial birds should also be taken into consideration by government agencies when recommending insecticides for grasshopper control and in choosing those for which the cost is to be subsidized. Similarly, municipalities should choose insecticides with the lowest toxicity to nontarget organisms for such applications as along roadsides and in pastures.

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4. THE IMPACT OF PESTICIDES ON THE ECOLOGY OF PRAIRIE-NESTING DUCKS

(P.K. Sheehan, A. Baril, P. Mineau, D.K. Smith, A. Harfenist and W.K. Marshall, Canadian Wildlife Service)

Introduction:

Approximately one quarter of the total North American duck population breeds in Canada's breadbasket -the prairies. Encroachment of agriculture on the waterfowl resource has been extensive and shows no sign of abating. Whereas physical disruption of the wildlife habitat has been all too visible, the possibly more insidious impact of pesticides on the quality of the wildlife habitat needs to be determined. As the habitat base keeps shrinking, the emphasis of managers will gradually change from the quantity of habitat remaining to the quality of what is left.

As we move away from the use of highly persistent and bioaccumulatory insecticides, such as organochlorines, to the current North American arsenal of organophosphates, carbamates, and more recently synthetic pyrethroids, it stands to reason that our approach to monitoring environmental quality has to change. No longer are measurable residue levels commensurate with probable impact. Therefore, the use of any species as a bio-indicator of environmental conditions becomes almost exclusively an exercise in population surveying and modelling.

The Wildlife Toxicology and Surveys Branch of the Canadian Wildlife Service looked at what is currently known of the effects of pesticides on waterfowl and tried to assess probable effects based on a knowledge of waterfowl biology and on the properties of pesticides currently in use.

Methodology:

We relied on the open literature as well as government reports and publications. Key individuals were contacted when written information was unavailable. Some of the extensive data sets used in our analysis include Canada Land Inventory, annual waterfowl surveys conducted jointly by the Canadian Wildlife Service and U.S. Fish and Wildlife Service and various agronomic censuses including the quinquennial effort by Statistics Canada. Some models were constructed to look at the probable effects of pesticides on duck nesting and survival.

Results and Discussion:

The report is too long to be adequately summarized here. It is structured in the following way:

1. Introduction
2. Waterfowl and prairie slough ecology
3. Waterfowl production - agriculture overlap
4. Pesticide use in the prairies
5. Pesticide delivery and potential for off-target contamination
6. Insecticide impacts on prairie sloughs
7. Herbicide impacts on sloughs and upland habitat
8. Impact scenarios - a quantification of the damage
9. Summary and recommendations

A number of important points emerged from this analysis. One was the paucity of adequate information to make an assessment of the possible effects of pesticides on the waterfowl resource. Because pesticides are seldom considered by wildlife managers, a number of opportunities for collecting some of the relevant information are wasted. The impact of insecticides and herbicides on the waterfowl resource is potentially very large. For example, one finding was that the number of breeding waterfowl directly exposed to insecticides in a year of large grasshopper outbreak is equivalent to the number harvested through hunting in the prairie provinces. Some of these insecticides present a definite toxic hazard to waterfowl. A number of insecticides also have the potential to reduce aquatic food supplies below starvation level in the case of young ducklings. The effects of herbicides on nesting cover in field edges and other non-crop areas are poorly documented but predictions made on the basis of existing data are worrisome because they show that herbicides could be a major cause of reduced waterfowl productivity.

In summary, this report makes the case that more emphasis should be placed on pesticides as a factor affecting waterfowl populations as well as the viability of their habitat.

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Carbofuran
Chlorpyrifos

5. GRASSHOPPER SPRAY SURVEY – SASKATCHEWAN AND ALBERTA (1986) D.J. Munro

Introduction:

During the summer of 1986, the Water Quality Branch undertook a survey to assess the presence and effect of grasshopper pesticides in aquatic ecosystems of southern Saskatchewan and Alberta. Collection and field extraction of 40-L water samples was undertaken at twelve sites in grasshopper-infested areas of Saskatchewan and Alberta. The extracts were analyzed for five insecticides and two breakdown products. Macroinvertebrates were sampled at six stream sites in Saskatchewan to examine possible effects of insecticides on these communities. Carbofuran and chlorpyrifos were found in low concentrations in the majority of samples. The concentrations that were found were all well below levels reported to be toxic to aquatic organisms. No change could be detected in the macroinvertebrate communities, suggesting no toxic effect of insecticides on the macroinvertebrate populations.

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6. SOUTH SASKATCHEWAN WATERSHED STUDY

(Dr. D. Waite and H. Sommerstad, Environmental Protection, Regina; Dr. R. Grover and Dr. L. Kerr, Agriculture Canada, Regina; Dr. N. Westcott, Agriculture Canada, Saskatoon)

Introduction:

The "South Saskatchewan Watershed Study" was designed to measure the movement of agricultural pesticides from target areas into a permanent body of water and to estimate their aquatic toxicity. Samples were analysed for: dicamba, bromoxynil, 2,4-D, trifluralin, triallate, diclofop-methyl, carbofuran, carbaryl, chlorpyrifos, dimethoate and deltamethrin by the Agriculture Canada Research Stations in Regina and Saskatoon. Information an aquatic toxicity of pesticides specific to the prairies is limited, and the objectives of this study were:

1. to determine on an annual basis the primary pesticides used in a contained agricultural watershed;
2. to measure movement of pesticides by spring run-off, aerial transport and groundwater, into a water body in the watershed;
3. to estimate the toxicological impact of those chemicals, individually and collectively, on representative aquatic biota; and
4. to delineate the contributing area and determine surface and groundwater contributions of pesticides to permanent water bodies.

Methodology:

The study area comprises approximately 2800 ha operated by 17 farmers and the city of Regina. Every year a survey is done to determine what crops were grown and which pesticides were used on each crop. This information is critical for the study.

Agricultural chemicals can move by the following atmospheric mechanisms: lateral movement of spray drift; attached to particles of soil eroded from treated fields; and evaporation from treated areas followed by direct deposition, rain wash-out or particle absorption and deposition. Atmospheric movement was measured by collecting dust, precipitation and direct aerosol deposition in specially constructed collectors. Quantities of chemical deposited were converted to deposition rates of $\mu g/m^2\text{-}d^{-1}$.

In Saskatchewan, 90% of the surface water movement occurs during a brief period in the spring. This water carries dissolved impurities, eroded soil particles, and dust which has collected on the snow during the winter. Spring run-off samples were collected from seven sites in the watershed.

There are two permanent water bodies in the watershed which receive water from surface run-off, rain and, possibly, groundwater. These ponds are too shallow to support fish, but contain apparently healthy populations of plants and invertebrates. Weekly water samples were taken from each pond in 1985 and 1986. Weekly groundwater samples were pumped from four cast-iron stand pipes sunk into the adjacent surficial aquifer. These samples represented water which accumulated during the week.

The toxicological impact of the pesticides on the local environment was estimated in two ways. Bottom dwelling animals (mostly insects) were collected and enumerated weekly to detect any sudden fluctuations in the population which might be attributed to toxic input from atmospheric sources. Precipitation samples were collected and assayed for the mutagenic potential with the Ames test, and tested for direct toxicity using *Daphnia* (water fleas), an alga, and bacteria (Microtox test).

Results and Discussion:

In 1985, five herbicides were identified in atmospheric samples. The maximum deposition rate was 4.32 $\mu g/m^2\text{-}d^{-1}$ of 2,4-D in late June and early July. In both years 2,4-D was the most frequent pesticide identified and diclofop-methyl the second most frequent. Dicamba, bromoxynil and triallate were also found. Carbaryl and carbofuran, insecticides used against grasshoppers, were detected in air samples.

Five herbicides were measured in the 1985 run-off. Diclofop-methyl occurred most often (35 of 37 samples) and triallate was the next most common (25 of 37 samples). The maximum estimated amount of herbicide from run-off was 2568.1 mg/h for diclofop-methyl. Most levels were considerably below this figure.

In 1985 none of the six herbicides or five insecticides were detected in groundwater samples. In 1986 no insecticides were detected; however, diclofop-methyl was found in 6 of 38 samples at the 0.1 to 4.9 ppb range. One sample also contained 2,4-D.

In 1985 eight of 32 pond water samples contained 2,4-D and two contained diclofop-methyl. In 1986 only four samples had positive results and these were all triallate. No insecticides were detected from either pond.

Despite considerable spraying in the area for grasshoppers, there were no catastrophic changes in the bottom dwelling animal populations in the ponds.

None of the precipitation samples were capable of causing mutagenic changes as determined by the Ames test. All of the samples, however, were toxic to at least two to the three organisms tested. All samples were toxic to *Daphnia* even when the rain water was diluted by 50%, and most were toxic when diluted to 25% of the original concentration. All samples were toxic to the algae, some at as low as 6.25% of the original concentration. Most samples were toxic to bacteria, some at as low as 5.63% of the original concentration. The cause of this toxicity has not yet been determined.

Conclusions:

1. Measurable amounts of pesticides are transported by spring melt waters and by atmospheric processes.
2. Despite these movements, ambient concentrations of pesticides in standing waters appear to be low and sporadic.
3. Despite heavy chemical use in the area, the shallow groundwater remains, largely, free of contamination.
4. Atmospheric depositions were toxic to bioassay organisms but not to the organisms living in the ponds.

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EP Interim Reports 1984 and 1985.

7. PESTICIDE CONTAMINATION OF THE LA SALLE AND ASSINIBOINE RIVERS IN MANITOBA

(S. Therrien-Richards)

Introduction:

The La Salle River is located within an intensely farmed fertile basin in south-central Manitoba. The natural flow in this stream is being augmented with water pumped from the Assiniboine River in an attempt to provide an adequate supply for domestic consumption, livestock watering and irrigation purposes. Concerns with regard to the presence of agricultural pesticides in this stream led to the initiation of the study.

The objective of this study was to determine the distribution of agricultural pesticides within the La Salle and Assiniboine Rivers in the La Salle watershed.

Methodology:

A farm survey of agricultural pesticide use within the La Salle River watershed was conducted to determine which pesticides were used most extensively. Based on the farm survey, all samples were analysed for bromoxynil, 2,4-D, MCPA, dicamba, diclofop-methyl, triallate and trifluralin. Water samples were collected from seven locations on the La Salle River and from two locations on the Assiniboine River once per month from August to December, 1984. Forage fish, aquatic plants and bottom sediment samples were collected on one occasion in August, 1984.

Results and Discussion:

Dicamba, bromoxynil, and 2,4-D were quantified in water samples from the La Salle River at concentrations ranging from 0.10 to 3.98 µg/L. Trifluralin and triallate were not detected in the water, but were quantified in forage fish and bottom sediment samples collected from both rivers. MCPA was not detected in any medium. No pesticides were detected in the aquatic plant samples.

The concentrations of pesticides in both rivers were below the maximum drinking water levels that have been established by Health and Welfare Canada, or where maximum concentrations have not been established, were less than the acceptable daily intake values set by the U.S. Environmental Protection Agency or by the World Health Organization. There is concern, however, with the presence of trifluralin and triallate in the sediment and fish.

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8. PERSISTENCE AND MOVEMENT OF PICLORAM IN A NORTHERN SASKATCHEWAN WATERSHED

(Dr. D. Waite, Environmental Protection, Regina; Dr. R. Grover, Agriculture Canada, Regina; Dr. A. Smith, Agriculture Canada, Regina)

Introduction:

Some concern has been expressed by the public over the contamination of water supplies by picloram sprayed to control brush. The large-scale application of picloram on a Dept. of National Defense weapons range in northern Saskatchewan provided an opportunity to monitor the persistence and transport of picloram under the influence of a northern climate. The objectives of this study were:

1. to study the leachability of the herbicide picloram (Tordon) in sandy soil;
2. to study the persistence of picloram in sandy soil; and
3. to monitor the residues of picloram in sediments and water in nearby lakes.

Methodology:

Following the application of picloram to the range at a rate of 3.38 kg/ha, a series of water wells were installed to sample groundwater, soil samples were taken from the range, water and sediment samples were taken from nearby lakes, and fish were caught. All of the samples were analysed for picloram residues to determine if it stayed in the soil or if it would drain through the soil into the lakes.

Results and Discussion:

The picloram applied to the range moved down into the sandy soil and entered the groundwater. Movement of the groundwater caused the chemical to enter a nearby lake. Due to poor water circulation and possibly continuing contamination from the range, the picloram remained in the water for nearly a year. No picloram was detected in fish, nor was any damage to aquatic vegetation noticed.

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EP Report Number W&NR 86/87-CP(EPS)-4

PESTICIDES PROGRAM IN THE ONTARIO REGION

1. PATHWAYS OF ORGANIC CONTAMINANTS IN FLUVIAL SYSTEMS (J.H. Carey)

Introduction:

The lampricide 3-trifluoromethyl-4-nitrophenol (TFM) is used in the Great Lakes for control of the sea lamprey (*Petromyzon marinus*). More than 1.25 million kg have been applied to Great Lakes tributaries since the program began in 1958. Studies of the degradability of this compound indicated that it is very resistant to chemical reactions and biodegradation. Laboratory studies into its photodegradation revealed that sunlight could degrade this compound into at least seven products. After confirming this photoreactivity in a treatment of an experimental pond, the decision was made to investigate a stream during an actual treatment.

The herbicide dinoseb (2-sec-butyl-4, 6-dinitrophenol) has been used in Canada on a variety of crops including potatoes on the east coast, peas and cereals throughout eastern Canada and berries and other crops in the Fraser River delta. Since it is a phenol, it is likely soluble enough to be mobile under field conditions. It may enter the surface waters in field drainage and shallow seepage. Since both dinoseb and TFM are nitrophenols, an investigation was initiated to determine if dinoseb would undergo photodegradation by the same mechanism as TFM.

The objective of this study was to complete work on photolysis of the lampricide TFM and initiate study of the photolysis of the herbicide dinoseb.

Methodology:

During the treatment of a small stream in eastern Ontario, samples of water were collected from upstream and immediately downstream of the treatment site. Further samples were collected over the next three days (as the TFM 'plug' moved downstream) and analysed for TFM and its degradation products.

A laboratory study into the mechanism of TFM degradation was conducted in collaboration with scientists from McMaster University. The effects of a variety of quenchers on excited state lifetimes and product quantum yields were determined.

Spectral characteristics of dinoseb were determined as a function of pH. Laboratory irradiations were conducted at 350 nm and dinoseb disappearance as a function of pH was monitored by spectrophotometry.

Results and Discussion:

Most of the laboratory work for the study of the mechanisms of the TFM photodegradation was completed and a draft manuscript prepared. Evidence was presented which suggests that the photodegradation of TFM involves photorearrangement to a nitrite ester followed by a variety of thermal reactions. After review of this draft manuscript, the study team decided that one final experiment was desirable to strengthen the case for the proposed mechanism. If feasible, this isotopic labelling experiment will be conducted in the coming year and, if successful, results will be incorporated into the manuscript which will then be submitted to a journal.

A laboratory study on the photolysis of dinoseb was initiated during the year. Since both dinoseb and TFM are nitrophenols, it was expected that the photolysis of dinoseb would be similar to that of TFM. In fact, both the chemical properties and photolysis mechanism of these two pesticides were markedly different. Further studies on the rates and mechanism of dinoseb photolysis are planned for the coming fiscal year.

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2. BIOMONITORING TECHNIQUES FOR PESTICIDES IN AQUATIC SYSTEMS (J.L. Metcalfe)

Introduction:

The unionid mussel, *Elliptio complanata*, was evaluated as a biomonitor for pesticides in the Yamaska River, Quebec, and in the South Nation River, a tributary of the Ottawa River. Mussels have been successfully used in the past as biomonitors for certain pesticides, particularly the persistent organochlorines. As such, they should be excellent candidates for the Ottawa River where chlordane, DDT and its metabolites, dieldrin, endrin, endosulfan, heptachlor, lindane and methoxychlor have been identified in river water. An on-going study to develop a general biomonitoring program for the Ottawa River was expanded in 1986/87 to include a pesticide site - the South Nation River which drains agricultural land from four Ontario counties. *E. complanata* is also under consideration as a biomonitoring organism for the relatively non-persistent pesticides used in the Yamaska River basin. Rapid uptake and excretion by aquatic organisms, and low bioconcentration factors have been demonstrated for pesticides such as aminocarb, atrazine and parathion. This does not preclude toxic effects, but makes the link between exposure and effects difficult to establish. Mussels are promising candidates for identifying the presence, levels, and trends of non-persistent pesticides because their elimination rates of xenobiotics are slow relative to fish and crustaceans.

A joint study with the Ontario Ministry of the Environment (MOE) to compare the potential of two benthic invertebrates, the leech *Nephelopsis obscura* and the mussel *Elliptio complanata*, as biomonitors for chlorophenols and dioxins in the Rainy River (NW Ontario) was also undertaken. These compounds had been identified in the river, downstream of two pulp and paper mills, in the previous year. In earlier work, MOE found mussels to be unsatisfactory for detecting chlorophenols in the environment. In contrast, NWRI's previous work with leeches has shown that these organisms bioaccumulate chlorophenols to levels from one to several orders of magnitude higher than fish or other benthic organisms.

The objective of this study was to develop biomonitoring techniques for determining the occurrence, levels and bioavailability of pesticides in the aquatic environment and for assessing the ecological/physiological effects of pesticides on aquatic biota.

Methodology:

Mussels from a pristine lake (Balsam Lake) were exposed for two months in cages at 11 sites in the lower Ottawa River, including sites upstream, downstream and in the South Nation River. In the Yamaska River, three cages of mussels were exposed for periods of two weeks, one month and two months in each of five tributaries known to be contaminated with agricultural pesticides. The exposure period represents a substantial portion of the growing season, and any changes in pesticide use with advancing season should be reflected in our samples. All mussels from both studies were frozen and are awaiting analysis, with the exception of a small number of samples from the Ottawa River study which were analysed using resources received by the WQB-OR from Pestfund (the Ottawa River study is a joint NWRI/WQB-OR study).

Cages of leeches and mussels were exposed together for three weeks at 17 sites along the Rainy River between Rainy Lake and Lake of the Woods. The feasibility of caging leeches was evaluated, and samples of both leeches and mussels have been submitted to the WQNL and MOE laboratories for the analysis of chlorophenol and dioxin residues.

Results and Discussion:

All mussels survived their exposure periods in the Yamaska and Ottawa Rivers. Only two cages in the Ottawa River and none in the Yamaska River were lost to vandals. Preliminary results of the Ottawa River study have been reported elsewhere (WQB-OR's report to Pestfund) and will not be repeated here. The remaining samples from both studies will be analysed for pesticide residues in their tissues and will also be used for determining stress responses. Because mussels can survive long exposures under field conditions, stress responses indicative of local environmental conditions will have time to develop. Some responses which will be investigated are: differences in growth rates (shell measurements), changes in condition factors (e.g., body weight, % lipids), and changes in amino acid ratios. The latter have been observed in marine bivalves in response to a variety of pollutants.

The analyses of chlorophenol and dioxin residues in leeches and mussels from the Rainy River have not yet been completed. Leech caging experiments were found to be feasible, with 80% survival or better after three-week exposure at the sites furthest downstream. However, high rates of mortality occurring not only in the vicinity of the pulp mills but also at the upstream control sites suggested that some aspects of water quality unrelated to pulp mill effluents was responsible. As leeches are known to be very sensitive to changes in water hardness, and as hardness increases in a downstream direction in the Rainy River, this may have been the factor responsible. The leeches used in the study were not native to the area, and the use of resident species is recommended wherever possible in future studies. Based on these techniques and recommendations, MOE conducted a successful study later in 1986 using caged leeches to identify the occurrence and distribution of chlorophenols downstream of a wood preservative plant.

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3. EFFECTS OF PESTICIDES ON ALGAL PHOTOSYNTHESIS AND ZOOPLANKTON ASSIMILATION (D.R.S. Lean)

Introduction:

The impact of pesticides on lake ecosystems may be expressed in many ways and consequently no simple test can provide adequate screening. The following method was developed to measure physiological effects on both algae and zooplankton. Initial experiments were conducted to evaluate selected pesticides (2,4,-D, dinoseb, deltamethrin and cyhalothrin) on photosynthesis by the assemblage of algae in the Bay of Quinte, Lake Ontario and on the assimilation of the labelled photosynthate by daphnids. For the phytoplankton, not only was the total ^{14}C-bicarbonate measured but also the synthesis of the subcellular fractions of carbohydrate, lipid, and protein. Pesticides may alter an animal's activity (in this case feeding) or its ability to assimilate and metabolize. These effects were monitored by measuring the quantity and form of the labelled photosynthate which was taken up by the zooplankter (*Daphnia galeata mendotae*).

The object of this study was to develop an index for lethal and sublethal stress from pesticides on phytoplankton and zooplankton in lake waters.

Methodology:

Lake water was prefiltered to remove existing zooplankton and 20 adult daphnia readded to samples contained in 300-mL BOD bottles spiked with ^{14}C-bicarbonate and a range of pesticide concentrations (in duplicate). Phytoplankton and zooplankton samples were collected following a 12-hour exposure at optimal light intensity and again after 12 hours in the dark. The samples were frozen for radioassay and subcellular fractionation into carbohydrate, protein, and lipid.

Results and Discussion:

The rate of photosynthesis was determined for each of the samples. For example, 2,4-D, at high concentrations inhibited the total carbon fixed but the subcellular distribution was constant. Alternatively, there was less inhibition with dinoseb but protein and lipid synthesis was altered. The lethal effects of these herbicides on daphnia require further study. The insecticides deltamethrin and cyhalothrin did not affect the phytoplankton but the rate of assimilation of the labelled photosynthate was reduced even at sublethal concentrations.

This method provides information on total photosynthesis as well as protein, carbohydrate and lipid synthesis in plants. Inhibition of protein synthesis in plants or assimilation of protein by animals would indicate a reduced growth rate and probably result in the exclusion of the organism from the ecosystem. Lipids produced by algae tend to concentrate non-polar pesticides, they then are assimilated for egg production by zooplankton. Further work on pure cultures will continue with the aim to standardize a lake community.

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4. THE EFFECT OF DISSOLVED ORGANIC MATTER ON THE BIOACCUMULATION OF SYNTHETIC PYRETHROIDS BY THE CLADOCERAN, *Daphnia magna* (K. Day)

Introduction:

The synthetic pyrethroids (e.g., permethrin, cypermethrin, deltamethrin and fenvalerate), are a group of insecticides currently registered and widely used on many agricultural crops in Canada. As a group, the pyrethroids are classified as moderately persistent, hydrophobic chemicals with low mammalian toxicity but high toxicity to fish and many aquatic invertebrates. The accidental introduction of the synthetic pyrethroids into the aquatic environment through overspray, drift or runoff may result in these chemicals becoming quickly adsorbed to living and non-living particulate matter and/or colloidal or dissolved organic matter. It is unknown whether or not such adsorbed chemicals are bioavailable to aquatic organisms either to exert a toxic effect or to bioaccumulate or both.

The objective of this study was to determine the chemical distribution of three synthetic pyrethroids in water containing various levels of dissolved organic matter and the effects of these levels on the uptake and bioaccumulation of the chemicals by the cladoceran, *Daphnia magna*.

Methodology:

Several studies were conducted to measure the adsorption of three synthetic pyrethroids (deltamethrin, fenvalerate and cyhalothrin) to dissolved humic material (DHM) (Aldrich Humic Acid) and to determine the effects of this adsorption on the bioaccumulation of the pesticides by *Daphnia magna*. Groups of adult *D. magna* were exposed to the radio-labelled pesticides (0.2 µg deltamethrin/L, 2.3 µg fenvalerate/L and 0.9 µg cyhalothrin/L) in aqueous solutions. Selected concentrations were below the 24-h LC_{50}. Water from Lake Ontario with added concentrations of DHM (0, 0.5, 1.0, 5, 10, 15, 30 mg/L) was filtered through 0.3 µm Gelman AE membrane filters. Experiments were run using 300-mL BOD bottles rotating on a wheel at 21°C in the dark. After 24 hours of exposure, the amount of each pesticide found in the water, adsorbed to the sides of the glass bottles and accumulated by the animals was determined by liquid scintillation counting.

Results and Discussion:

The three pesticides were found to adsorb to the sides of the glass containers at all concentrations of DHM; however, the greatest adsorption occurred in the controls. For example, the percent of applied radioactivitiy on the glass in the control bottles was 16.9%, 8.6% and 4.7% for deltamethrin, fenvalerate and cyhalothrin, respectively, compared to 9.3%, 3.4% and 0.5% on the glass in bottles containing 30 mg/L DHM. The percent of applied radioactivitiy remaining in the water increased as DHM increased; 14C-deltamethrin increased from 59.6% to 79.2% in 30 mg/L DHM; 14C-fenvalerate increased from 74.1% to 86.5% in 30 mg/L DHM;and 14C-cyhalothrin increased from 83.3% to 98.2%. These observations suggest that the presence of dissolved organic material such as humic acids increases the surface area available for adsorption of lipophilic compounds (hydrophobic chemicals).

The binding of the synthetic pyrethroids to DHM directly affects the accumulation of these chemicals by *D. magna*. The percent of the applied radioactivity found in the animals decreased from 2.7% to 0.4% for deltamethrin; 3.1% to 0.6% for fenvalerate; and 3.8% to 0.5% for cyhalothrin as DHM increased. The amount of actual chemical in the bodies of the animals decreased from 0.31 to 0.04 pmol deltamethrin/g wet weight, 3.40 to 0.72 pmol fenvalerate/g wet weight, and 1.55 to 0.22 pmol cyhalothrin/g wet weight. These results suggest that a contaminant bound to DHM greatly reduces the bioavailability for uptake by organisms compared to unbound contaminants.

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5. PYRETHROIDS METHODS DEVELOPMENT (H.B. Lee and A.S.Y. Chau)

Introduction:

Pyrethrins, extracts of the naturally occurring pyrethrums, have good insecticidal properties and low mammalian toxicity. They are, however, highly unstable in light and degrade rapidly making them not useful for agricultural applications. Since the discovery of natural pyrethrins during the 19th century, there has been much interest in the development of synthetic pyrethroids with similar structures and properties. By 1973, several new compounds which were more stable yet retained many of the favourable characteristics of the natural pyrethrins, were developed. Among these, permethrin, cypermethrin, deltamethrin, and fenvalerate, have received the greatest attention. These pesticides give adequate control of insects in agriculture, have low mammalian toxicity and are of low to moderate persistence. These pyrethroids are being considered as replacement compounds for organochlorine, organophosphorus and methylcarbamate insecticides because of their desirable features; therefore, it is important to have adequate methodology for routine analysis of these chemicals. Synthetic pyrethroids have been registered in Canada for many uses including the control of fruitworm, potato beetle, corn borer, leaf miner and cutworm in fruit and vegetable crops.

The final goal of this study is to develop methods for the routine analysis of the four synthetic pyrethroids, (i.e., permethrin, cypermethrin, deltamethrin and fenvalerate); as well as the neutral metabolites, (i.e., 3-phenoxybenzyl alcohol (PBalc), 3-phenoxybenzyl aldehyde (PBald)); and acidic metabolites (i.e., 3-phenoxybenzoic acid (PBacid), and 3-(2,2-dibromovinyl)-2, 2-dimethylcyclopropanecarboxylic acid (DBCA)), in water and sediments. For this reporting period, the feasibility of several analytical approaches for these pesticides was evaluated.

Methodology:

Water samples were extracted from dichloromethane and each extract was halved. The first half was analysed for the parent pyrethroids as well as their neutral metabolites. The other half was analysed for the acidic metabolites by the formation of their PFB ester derivatives.

Results and Discussion:

Chromatographic separation for a mixture of the parent pyrethroids was accomplished with a 12-m, OV-1 fused silica capillary column. Using a suitable temperature program, nine peaks were observed for the mixture due to the presence of isomeric species. Two of them were attributed to permethrin (cis- and trans-isomers), four to cypermethrin, two to fenvalerate, and one to deltamethrin. Their electron capture detection (ECD) response factors were also estimated. Because of their low volatilities, very high column temperatures (> 260°C) were required to chromatograph the parent compounds. When splitless injections were made on a capillary column, some memory effect due to carry over of the pyrethroids from one sample to the next was experienced.

A method for analysing the four synthetic pyrethroids in water at sub-ppb level was evaluated. This method involved solvent extraction of the pesticides by dichloromethane (DCM) and cleanup of the sample extract on a 10% deactivated Florisil column. Because of the relatively high polarity of these pesticides, the pyrethroids were eluted in 1% acetone in hexane fraction. Quantitative recovery of the pyrethroids was obtained from water samples fortified at 0.3 to 0.5 µg/L levels. Further work is required, however, to evaluate the recovery of these compounds at even lower levels.

Another method for the analysis of the pyrethroid acidic metabolites, (i.e., PBacid and DBCA) was also developed. The acids were extracted from water by DCM after the sample was acidified to pH < 1. The extract was then derivatized into the ECD-sensitive PFB esters to obtain the required sensitivity for the detection of a non-halogenated acid such as PBacid at low levels. The esters were further cleaned up on a 5% deactivated silica gel column before the toluene recovery of PBacid and DBCA at 0.5 to 0.7 µg/L levels; however, further evaluation of the method at other levels is required. Because of interference in the derivatized products, a GC-MSD method for the confirmation of products was also developed.

Two methods were evaluated for the analysis of the neutral metabolites, PBald and PBalc. One involved the HPLC technique using a reversed-phase C18 column for the separation of the metabolites and a variable wavelength UVD for quantitation. Although this combination was demonstrated to be sensitive (D.L. 50 ng/L) it was not specific or selective enough for the analysis of PBald and PBalc in natural water samples due to interference of coextractives. The other method involved the detection of these compounds using a capillary column interfaced to a MSD. By monitoring the molecular ions and a few characteristic ions, this highly selective method was also sensitive. Based on a concentration factor of 1000, the detection limits for PBald and PBalc were 5 ng/L and 10 ng/L, respectively. Using DCM, extraction recoveries of these compounds were also better than 85%.

These methods have been applied to the analysis of deltamethrin and its neutral and acidic metabolites in a number of samples collected in Prince Edward Island after spraying of the pesticide. It should be emphasized that these methodologies are only preliminary. Further work is required to validate the methods at different levels as well as to develop similar analytical methods for these compounds in sediment samples.

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6. REDUCTIVE CHLORINATION OF PESTICIDES (R. Baxter)

Introduction:

Some observations have been made on pesticides as part of a wider study on the reductive dechlorination of environmental contaminants. Many substances that are relatively persistent under oxidizing conditions undergo at least primary degradation under reducing conditions. Reductive dechlorination (i.e., the replacement of a chlorine atom by a hydrogen atom), is one of the most important reactions involved in such degradations.

One mechanism for reductive dechlorination involves the reaction between a chlorinated compound and a reduced iron porphyrin such as hematin. In the presence of a suitable reducing agent, the oxidized iron porphyrin produced in the reaction is reduced again, so a small amount of iron porphyrin can serve as a catalyst to dechlorinate a large quantity of starting material. Since iron porphyrins occur widely in biological materials, it seems likely that this process may be of environmental significance in anoxic soils and sediments.

The objective of this study was to determine the reductive chlorination of pesticides in water.

Methodology:

The compounds under test were incubated with hematin in the presence of sodium dithionite as a reducing agent. At intervals, samples were extracted and the extracts were analysed by gas chromatography.

Results and Discussion:

The pesticides that were found to be degraded were methoxychlor, lindane, and the cyclodiene insecticides, aldrin, dieldrin, and heptachlor. Aryl chlorides such as chlorophenols do not appear to react. The scope of this particular reaction has now been sufficiently defined, and subsequent investigations will involve possible dechlorination reactions by certain species of microorganisms.

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7. OCCURRENCE, PERSISTENCE AND FATE OF TRIBUTYLTIN IN CANADIAN WATERS
(R.J. Maguire)

Introduction:

In Canada, tributyltin is used in various compounds and formulations mainly as an antifouling agent in some paints for boats, ships and docks. It is also used as a general lumber preservative and as a slimicide in cooling water. It is one of the most toxic chemicals to fish of the 1000 or so chemicals which have been identified in the Great Lakes. By virtue of its high aquatic toxicity it is the most prominent of the organotin compounds for which environmental and human health hazard assessments were called under the Environmental Contaminants Act in 1979.

The objective of this study was to determine the hazard posed to the aquatic environment through the use of the highly toxic antifouling pesticide tributyltin.

Methodology:

Analytical methods for tributyltin were developed for water, sediment and tissue. A survey of 300 locations across Canada was conducted to determine its presence in water and sediment, and an estimate of its persistence in aquatic environments was made after experiments were performed on physical, chemical and biological pathways of degradation.

Results and Discussion:

In Canada, tributyltin has been found mainly in harbours, marinas and shipping channels, which is consistent with its use as an antifouling agent. In water, its concentration in some locations was high enough to cause concern with regard to chronic toxicity or effects in sensitive organisms. It has also been found in mg/kg concentrations in harbour sediments, but the toxicological significance of sediment-associated tributyltin is unknown. Biological degradation in water and sediment appears to be the rate-limiting factor which determines the persistence of tributyltin in aquatic environments, and based upon laboratory experiments, the half-life in fresh water at 20° C is estimated to be of the order of six weeks to a few months. Methylation of tributyltin and its degradation products in aquatic environments has been demonstrated, but it does not appear to be a significant pathway of transformation in fresh water.

This is a final report. These results have been communicated by the Commercial Chemicals Branch of Environment Canada to the Department of Agriculture, and the Department of Agriculture will require that tributyltin-containing antifouling paint formulations be registered under the Pest Control Products Act.

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8. ATMOSPHERIC CONCENTRATIONS OF IN-USE PESTICIDES

(D.A. Lane & W.H. Schroeder (Scientific Authority) AES; N.D. Johnson (Contractor; Project Leader) Ontario Research Foundation; W.M.J. Strachan (Principal Scientist) National Water Research Institute)

Introduction:

The federal regulatory re-evaluation process applied to in-use pesticides requires up-to-date information on their presence (or absence) in the atmosphere as well as in other compartments of the environment. In this connection, it is important to possess information on current environmental concentrations of in-use pesticides in ambient air, including their temporal (seasonal/annual) and spatial variability. Such environmental data - obtainable at present only through field measurement programs - are also essential for mass balance calculations as well as the construction and validation of mathematical or conceptual models capable of describing, and ultimately predicting, the behaviour and fate of pesticides released into the environment. In addition to information on actual atmospheric concentrations of registered pesticides, knowledge regarding their gas-phase to particle-phase distribution (partitioning) in ambient air is necessary for adequate assessments of either potential human health effects or environmental behaviour, impact and ultimate fate of airborne pesticides.

The objective of this study was to determine gas-phase and particulate-phase concentrations of lindane and other persistent chlorinated organic compounds in ambient air in southern Ontario and at a remote location in central Ontario.

Methodology:

In the current phase of this project, a new sampler (developed for the Atmospheric Environment Service (AES) by the Ontario Research Foundation) was evaluated under a range of environmental conditions at several different locations in Ontario. When used in conjunction with a conventional dichotomous air sampler, this prototype sampling device is capable of determining the gas- and particulate-phase concentrations of several persistent organochlorine compounds in air simultaneously. This sampler comprises a diffusion denuder assembly (for trapping the vapour-phase components of the target substances) integrated into a dichotomous sampler (for collecting pesticides associated with fine and coarse particulate matter in the atmosphere). The initial development and laboratory testing/evaluation of this unit has been reported previously.[1,2,3]

The target compounds selected for the field measurements performed during 1986/87 fiscal year were: lindane (gamma-hexachlorocyclohexane), alpha-hexachlorocyclohexane (HCH) and hexachlorobenzene (HCB). These persistent organochlorine compounds are found consistently in rainwater and other environmental samples,[4,5] but information on their presence in the atmosphere at Canadian locations is sparse. In this study, field measurements (involving replication of the sampling and analysis steps in the overall measurement procedures) were conducted at several locations in southern Ontario and at a remote (background) site in the Turkey Lakes watershed north of Sault Ste. Marie.

Results and Discussion:

Results obtained during the field studies performed during the 1986/87 fiscal year are summarized in Table 1. The first set of measurements were taken during July 1986 in the western portion of Lake Ontario. Air sampling and meteorological equipment was operated simultaneously on the shoreline near Niagara-on-the-Lake and on board the CSS Bayfield (a CCIW Great Lakes research vessel) while it was anchored approximately 5 km offshore. Similar onshore/offshore measurements were conducted in the eastern part of Lake Ontario near Picton and an integrated sample was collected on the ship while it was traversing Lake Ontario between the western and eastern sites. Other field measurements in southern Ontario were made at Sheridan Park in Mississauga (during the autumn of 1986 and the winter of 1987) and in Stoney Creek (near Hamilton) at a site approximately 800 metres from an agricultural chemical producer (during the early part of the winter).

Air concentrations of α-HCH, γ-HCH and HCB were generally in the sub-nanogram per cubic metre (of air) range for the measurements performed at all of the sites. These findings are consistent with values reported from other studies. Lindane (γ-HCH) concentrations were about an order of magnitude lower than either α-HCH or HCB concentrations and were frequently at or near the detection limit of the analytical method used (dual column capillary gas chromatography with electron capture detection). The higher abundance of α-HCH relative to lindane may reflect environmental (perhaps photochemical) transformation of lindane. On the basis of autumn and winter measurements at the same location, the air concentrations of all three target compounds were found to decrease with decreasing temperatures.

From the results of the air measurements made so far with the GAP sampler it appears that the substances being investigated occurred predominantly in the vapour phase during warm weather conditions. However, under winter conditions (at the Sheridan Park site) a greater fraction of these high molecular weight, semi-volatile pesticides appeared to be associated with the airborne particulate matter.

For the studies around Lake Ontario and the Turkey Lakes watershed, atmospheric measurements were supplemented with determinations of the target compounds (as well as other organochlorine pesticides) in samples of lake surface water, suspended solids and other pertinent environmental matrices. These measurements, carried out under the direction of Dr. W. Strachan from the National Water Research Institute at Burlington, are the subject of a separate report.

TABLE 1 SUMMARY OF TARGET COMPOUND MEASUREMENTS

Location	Test Series	Average Air Concentration (ng/m^3)			Average Particulate-Associated Fraction by Denuder Difference (%)		
		HCB	α-HCH	γ-HCH	HCB	α-HCH	γ-HCH
Onshore/ Offshore:	Land West	0.3	0.7	<0.03	-	-	-
	Ship-West	0.2	0.4	0.06	6	14	~45
	Land-East	0.3	0.3	<0.03	0	-	-
Lake Ontario	Ship-East	0.3	0.5	0.07	2	8	~2
	Ship-Moving	0.2	0.5	0.06	0	5	~2
Turkey Lakes	Set 1	0.2	0.5	~0.04	0	10	~0
	Set 2	0.1	0.3	~0.04	5	5	~0
	Set 3	0.1	0.3	0.1	5	0	~0
Sheridan Pk. (Mod. Temp.)	Set 1	0.2	0.4	0.1	17*	18*	~23*
	Set 2	0.2	0.3	~0.04	4	6	~20
	Set 3	0.1	0.3	0.06	14	8	67
Sheridan Pk. (Low Temp.)	Set 1	~0.07	<0.03	<0.04	~100*	-	-
	Set 2	0.08	0.1	<0.02	~15	21	-
	Set 3	0.1	0.1	<0.02	~51	35	-
Stoney Creek (Near Source)	Set 1	0.1	0.1	0.1	~73*	28*	10
	Set 2	0.2	0.2	0.1	32	1	0

* Contamination suspected in at least one collection medium component in deriving these values.

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9. LIDAR MAPPING OF AERIAL SPRAY (R. Hoff, F. Froude, R. Mickle, Atmospheric Environment Service, Downsview, Ontario)

Introduction:

Sensitivity modelling studies have indicated that in forestry spraying, the "effective release height" is the single most dominant factor in determining deposit to the target area. The lifetime of the vortex is strongly dependent on stability and background turbulence. LIDAR mapping of the spray provides the capability to observe the vortex breakdown and subsequent release of spray material for dispersion.

The objective of this study was to better understand the vortex breakdown and subsequent release of spray material for dispersion during the aerial application of pesticides.

Methodology:

A scanning LIDAR system has been developed to map the spray cloud from release to impaction whether at forest top or at the ground. A 100 mJ Neodymium - YAG laser (1.064 μm) has been mounted in conjunction with a 35 cm Celestron Cassegrain Telescope (two milliradians field of view) into a cradle which can be scanned to map the spray cloud. A pulse length of ten nanoseconds at a repetition rate of 10 Hz with a maximum beam divergence of one milliradian translates into a spot size < 1 m at 1 km. Data acquisition is achieved using a 200 MHz LeCROY Digitizer giving < 1 m resolution along the beam path. The full system is controlled from a PC-AT based computer. Software development has been designed to encompass a typical spray scenario where intensive mapping is carried out to 60 m above the canopy with a vertical resolution of 2 m and a horizontal resolution of 0.75 m. Cross-sections of the vortex pair during decent/decay requires approximately one second with a new cross-section available every six seconds. During cloud dispersion, the rate of data capture is decreased in order to follow the cloud for an extra two minutes up to 0.8 km down-range. Presentation of the data is in terms of vertical/downwind relative concentrations above the forest canopy.

Results and Discussion:

The technique has been used to map spray from an Agtruck fitted with four micronairs and an Ayres Thrust fitted with boom and nozzle. Both aircrafts were flown into a head wind of 5 to 6 m/s at 30 m above a grass field.

The released spray was mapped from release until ground impaction. Initially, the concentrated spray was observed wrapped into the trailing vortices. With vortex breakdown, the lateral/vertical spreading, vertical and horizontal transport were mapped.

The technique is to be extended to map ultra low volume (ULV) spraying above a forest canopy in the coming year.

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10. PESTICIDE AERIAL DRIFT MODELLING (Concord Scientific Corp.)

Introduction:

Aerial spraying of pesticides to protect forests and crops is difficult to control due to potential off-target drift of small spray particles under the influence of ambient wind and turbulence. Increasing the size of droplets reduces off-target drift; however, it also has the undesirable effect of reducing overall pest mortality on "knock-down", especially in forest applications where ultra-fine droplets are most effective. Mathematical modelling of the drift and settling of airborne pesticides is an important tool in defining the conditions necessary to maximize knock-down and minimize spray drift beyond the target zone. A successful model needs to take into account the complex behaviours of spray droplets in the atmosphere. Air motions generated by the spray aircraft and the turbulence and mean motions of the lower atmosphere have the greatest influences. Few models exist that address all the significant phenomena affecting spraying dispersion and deposition. The major strengths and weaknesses of existing models were identified in this study. The methodology applied to this end and the major findings of the project are described in the following.

The objective of this study was to conduct an objective scientific assessment of the fundamental strengths and weaknesses of existing forest pesticide spray drift and deposition models, and to design, implement and evaluate an enhanced model incorporating state-of-the-art knowledge. A modelling tool that could be confidently applied for assessment purposes, reducing the difficulty and cost of pesticide regulatory re-evaluation programs was to be developed.

Methodology:

The model examination methodology included both theoretical and practical application aspects. The theoretical evaluation consisted of an extensive review of the various sub-models of three existing models (FSCBG[1], AGDISP[2], PKBW[3]), from the perspective of fundamental conservation laws and state-of-the-art knowledge, through a supplementary literature review.

To test application performance, models were run on a computer for selected test cases. The test cases corresponded to actual field trials from several data sets that were identified through a separate literature review. For this purpose, the FSCBG and AGDISP models were obtained from their original developers, and implemented on microcomputers. The PKBW model was already available. Model evaluation proceeded based on an intercomparison of results and the theoretical strengths of sub-models within each model.

Results and Discussion:

The model evaluation procedure indicated that the AGDISP model, based on its fundamental strengths and practical applicability, was a suitable framework on which to build an enhanced model. The FSCBG model was deemed to be weaker due to its Gaussian treatment of above-canopy dispersion, and the oversimplification of the aircraft wake effects. The PKBW model, utilizing the ARAP-VORTEX WAKE[4] code, which treats the wake effects in a very detailed manner, requires large computing sources. This makes it impractical to easy access for regulatory applications unless significant work is done in parameterizing the vortex wake. AGDISP, on the other hand, already has such parameterization built in and has the strong framework, but lacks an in-canopy foliage deposition sub-model, which is a major strength of the PKBW model. Therefore, for the enhanced model, it was decided to build PKBW's foliage deposition formulation into the AGDISP framework.

The field data sets identified as being the most suitable for model evaluation purposes, mainly due to their completeness, were the orchard spray trials at Withlacoochee, FL(Feb.,1980)[5], the Dunphy, N.B. spray trials (1984 and 1986)[6] and the agricultural spray trials, Mill Cove, P.E.I. (summer ,1986)[6].

Comparisons of model results with field data indicated that FSCBG can predict excessive oscillations in downwind canopy-top deposition profiles and can significantly under-predict ground deposition within the canopy. Quite expectedly, AGDISP over-predicts ground deposition due to its lack of a foliage deposition module.

Model input requirements indicate the need for specific variables to be measured during field trials, namely, aircraft height/type; spray spectrum and formulation; and meteorology including wind profile to twice aircraft height, turbulence at aircraft height, humidity, temperature and in-canopy wind profiles. Some shortcomings of the field data were identified as worthy of attention from workers in the area of data collection: a standardized canopy characterization scheme and increased accuracy in spray fate closure measurements. Also, error bounds on all measurements are essential for proper model evaluation.

References:

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2. Bilanin, A.J. and M.E. Teske, "Numerical Studies of the Deposition of Material Released from Fixed and Rotary Wing Aircraft," NASA Contractor Report 33779 (March, 1984).
3. Basak, N. "Lagrangian Simulation of Forest Pesticide Spray Dispersion and Deposition," M.Sc.Eng. Thesis, Dept. of Chemical Engineering, University of New Brunswick, Fredericton, N.B. (1985).
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6. Riley, C.M., "Estimating Drift of Off Target Aerial Deltamethrin Sprays", for EPS, Report No. C/86/102 (1986).

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11. ATMOSPHERIC LOADING: ATMOSPHERIC TRANSPORT AND DEPOSITION OF TOXAPHENE INTO THE GREAT LAKES ECOSYSTEM (Dr. E.C. Voldner, Atmospheric Environment Service, Downsview, Ontario)

Introduction:

Available data indicate that a number of toxic chemicals are transported via the atmosphere to regions remote from their use. As an example toxaphene, primarily used in the southern United States, has been detected in air and precipitation over the North Atlantic and in the Great Lakes basin. It has been found in fish and water in the Great Lakes and in peat bogs across eastern Canada.

At present it is difficult to quantify the atmospheric input of toxic chemicals to the Great Lakes. Previous estimates are generally based on a few measurements of ambient air concentrations and concentrations in precipitation, either in the basin or perhaps some remote area, which are then extrapolated in time and space.

In cooperation with Argonne National Laboratory, the Atmospheric Environment Service has developed a long-range transport model capable of simulating transport, dispersion and deposition of selected pesticides. With the aid of this model deposition of toxaphene to the Great Lakes and their basins was determined and the presence of toxaphene over the North Atlantic was explained. Two periods (1976 and 1980) with significantly different use patterns were simulated. Predicted concentrations in air and precipitation compare favorably with measurements.

It has been shown that several priority toxic chemicals enter the Great Lakes via the atmosphere. However, the amount of atmospheric loading, its significance relative to other inputs and its important sources are not known. Design of effective control policies and strategies is therefore difficult. In this ongoing project, toxic chemicals (priority and emerging) will be assessed to determine the importance of atmospheric transport, transformation and deposition to the Great Lakes ecosystem and potential sources of emissions.

Methodology:

To mathematically simulate the atmospheric deposition of toxaphene to the Great Lakes and their basins, the atmospheric pathway of the pesticides from its sources to its sinks must be determined. This requires quantification of emissions and simulation of aerial transport, dispersion, transformation and removal processes.

The model is Lagrangian and assumes linear physical and/or chemical transformation processes. Horizontal dispersion is parameterized from the distribution of trajectory ensembles, vertical dispersion and dry deposition are calculated as a function of emission layer and time since release in a one-dimensional vertical integration. Wet deposition is a function of precipitation intensity and amount. Eddy diffusivity, dry deposition velocities and chemical transformation rates vary diurnally and seasonally, while analyzed wind and precipitation fields across North America, required meteorological input, are supplied on a 6-h interval.

Since the model requires information of emission amount as well as time and location of emissions, a gridded toxaphene inventory was compiled. The inventory is based on information on use-pattern, methods and time of application, predictions from spray models, experimental studies on volatilization as well as information on residence time and fate in soil. It is assumed that 50% of applied toxaphene is emitted in the summer months and 10% in the early spring.

Preliminary Results and Discussions:

Analysis of trajectories clearly illustrates the potential exposure of the Great Lakes ecosystem to pollutants in the southern U.S.A. Based on the assumed emission of toxaphene, the model predicted that in 1980 and 1976 approximately 60% of the emitted toxaphene was deposited within North America. The remainder left the continent primarily over the east coast. Transport to the North Atlantic is supported by published measurements by other researchers.

Total deposition to the Great Lakes was in the range 4 to 10 kt in 1980. Wet deposition accounted for 70 to 80%. Lake Michigan received the largest deposition. Deposition to Lakes Superior and Erie were essentially the same, but lower than Lake Michigan. The deposition fluxes over the Lake Erie were relatively high, while the surface area of the lake is small. For Lake Superior the converse was true.

The average air concentrations over the lakes were generally below 1 ng/m^3 during early spring and 1 to 2 ng/m^3 during summer. The values are comparable to the few measurements found in literature.

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12. ATMOSPHERIC LOADING: EMISSION INVENTORIES OF TOXIC CHEMICALS (Dr. E.C. Voldner, Atmospheric Environment Service, Downsview, Ontario)

Introduction:

The presence of toxic chemicals in the Great Lakes ecosystem represents an issue of major concern under the United States - Canada Great Lakes Water Quality Agreement. Available data on a number of airborne toxic contaminants, both organic and inorganic substances, indicate that the atmospheric input constitutes a substantial and perhaps even a major route of entry to the Great Lakes ecosystem.

It is, therefore, of interest to:

1. determine annual deposition of selected nutrients, trace metals and toxic organic compounds to the Great Lakes and their basins;
2. determine temporal trends in deposition of these species; and
3. provide information on the presence/absence of toxic organic compounds and trace metals in ambient air and precipitation (and hence deposition) within the Great Lakes basins and thus augment an early warning system of emerging problems within the lakes ecosystem.

To fulfill the objectives is a formidable and costly task and requires an integrated monitoring, modelling and research effort. Information on location and amount of emission from atmospheric sources is essential. Emissions estimates alone serve as indicators of the significance of atmospheric loading relative to other sources (such as direct industrial discharge to the lakes); and provides guidelines for which compounds to measure in the atmosphere (emerging problems), which sources or source categories to control and for interpretation of trends in biotic uptake and contaminations of sediments. Emissions estimates are necessary inputs to models for quantification of deposition, establishments of trends (historical and predicted), and for determination of source/receptor relationships. Trend analyses are important for understanding and predicting response time of the lakes ecosystems to changes in pollutant loadings.

Pollutants, originating from anthropogenic and natural sources, are introduced into the atmosphere through primary and secondary emissions. Primary emission includes direct emission from such sources as: industrial stacks, incineration, residential chimneys, and forest fires. For pesticides it includes losses to the atmosphere through direct application of the pollutant and through volatilization of the pollutants from crop and soil during a relatively short period after application. Secondary emission includes recycling of material through resuspension and volatilization of previously deposited material. Pollutants can also be formed through chemical/photochemical reactions.

Once emitted into the atmosphere the pollutants are subject to transport, dispersion, physical/chemical transformations and scavenging through wet and dry deposition processes. The distance from actual emission to removal (source/receptor) is a function of parameters such as: effective height of release, meteorological conditions, and properties of the pollutants. Many pollutants of concern to the Great Lakes ecosystem are persistent, slowly scavenged from the atmosphere and subject to long range transport. Information on emissions of chemicals not only in the Great Lakes basin, but in North America and indeed in the Northern Hemisphere, therefore, may be of importance.

Methodology:

Information on emission was obtained from various organizations, from published papers and reports.

Preliminary Results and Discussions:

Information retrieved by the Atmospheric Environment Service (AES) up to November 1986 is summarized in Table 1. A draft report, including updated emissions information, is scheduled for April 30, 1987. It should be noted, that in most of the studies previously made, emissions have been estimated on an aggregate basis (i.e., by province and sector). Where information, such as source test data, were available, estimates have been made by combining this information with less specific, sector data. As such, the national and provincial emission estimates are not capable of fully supporting modelling activities, that require gridded and/or plant specific data. Emissions estimates of pesticides are essentially nonexistent. Information of pesticide usage is difficult to obtain. In Canada detailed usage is classified information.

TABLE 1 SUMMARY OF EMISSIONS INFORMATION RETRIEVED

	Pb	Cd	Hg	As	PAH	PCBs	PCDD PCDF	Pesticides
Global	X							
U.S. Total	X	X	X	X	X			
Sector	X	X	X	X	X			
State	X	X	X					
High Resolution	X							
History	X							
Projection	X							
Quality	G	P	P	P	P			
Canada Total	X	X	X	X	X		X	
Sector	X	X	X	X	X		X	
Province	X	X	X	X				
High Resolution	X	X						
History	X							
Projection	X							
Quality	G	G	G	P	P		P	
Consumption/ Prod/Sales								
U.S.						X		X
Canada						X		X
Storage								X

X = Data available
G = Good
P = Poor

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PESTICIDES PROGRAM IN THE QUEBEC REGION

1. DOMESTIC PESTICIDES

Introduction:

On May 14, 1987, the community health department of Lakeshore General Hospital held a press conference to present a report entitled "The Use of Pesticides in Residential Areas in the Lakeshore Community Health Department Region". Environment Canada participated in carrying out certain aspects of the design and in the preparation of the study.

Methodology:

For the region served by the Community Health Department, pesticide sales outlets, the types of services offered to the public, and the main products used were specified. In addition, a survey of 277 households was conducted to determine activities relating to property maintenance, attitudes toward and knowledge of pesticides and the nature of pesticides stored in the home. Findings were that:

- the use of pesticides in residential areas is widespread in this region (8 out of 10 households);
- many products for which the expiry date has passed are found in the home;
- it is difficult for residents to obtain complete, satisfactory information.

Recommendations contained in the report were to:

1. inform residents of product recalls or revocation of approval because of health or environmental risks;
2. carry out an information campaign covering:
   - risks,
   - more rational uses, and
   - more judicious choices;
3. assist and encourage citizens to eliminate expired or useless pesticides; and
4. provide training for salespersons.

Future action:

By the Lakeshore Community Health Department: Collect pesticides and submit them to specialized companies (in Ontario) in the spring of 1987.

By other Community Health Departments: Conduct similar studies in other fields in order to verify the conclusions obtained for areas of different economic and social backgrounds. The Lanaudière Community Health Department, has approached the Quebec Department of the Environment in this regard.

Recommendations:

1. to attend (but not participate) in the May 14 press conference organized by the Lakeshore Community Health Department;
2. to continue to offer assistance (as far as we are able) to other community health departments to establish a more effective profile on the use of domestic pesticides; and
3. using the basic data collected, develop a communications and information plan for domestic pesticides.

Note: At present, the Quebec Department of the Environment does not give priority to domestic pesticides, focussing its efforts on agricultural and commercial pesticides.

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2. CARBOFURAN AND WATER QUALITY (Dennis Trotter, Monenco Consultants Ltd., Calgary, Alberta)

Introduction:

In Canada, water quality guidelines are used by provincial, territorial and federal departments for evaluating water quality problems and for formulating site-specific water quality objectives. These guidelines are developed to provide basic scientific information concerning the effects of water quality parameters on various uses and to ensure adequate protection of public water supplies, agricultural water supplies, aquatic life, wildlife, aesthetics and recreation, and water supplies for industrial uses (CCREM, 1987).

The aim of this project was to review the existing scientific and technical information on the insecticide, carbofuran, with respect to effects on water quality parameters. Specifically, the goal is to develop water quality guidelines for the identified water uses.

Methodology:

An extensive literature review of the use, the physical-chemical properties, the levels in water, sediment and biota, the environmental fate and persistence in soil, water, and sediment; and the toxicology of carbofuran was undertaken.

Results and Discussion:

The relatively high solubility of carbofuran coupled with its relatively low absorption capacity for soils and sediments permits natural surface waters to become a repository for excessive amounts of the insecticide escaping treated areas or accidentally introduced into aquatic environments. Upon reaching the aquatic environment, carbofuran's persistence is directly related to the pH of the water. Carbofuran is stable in acidic environments but subject to increasing chemical hydrolysis as the water becomes more alkaline.

The microbial population in water, sediments, and flooded soils is also an important factor in reducing the persistence of carbofuran. Several species of microorganisms have been isolated which are capable of degrading carbofuran under laboratory conditions. As well, several field studies (especially from Canada and the United States) have demonstrated both enhanced and accelerated microbial degradation of carbofuran in soils previously treated with carbofuran or with bacterial and organic amendments to the soil. Photodecomposition does not play an important role in the dissipation of carbofuran in either the soil or water environment.

Objectives or guidelines for the protection of aquatic life from the harmful effects of insecticides in general, usually specify the use of an application factor (e.g., 0.01 or 0.05) to be multiplied by specific 48-h or 96-h LC_{50} values for sensitive aquatic species. Given the available toxicity data and the proposed application factors, criteria for carbofuran in freshwater could range from 0.335 to 4.4 µg/L. A maximum acceptable carbofuran concentration of between 15 and 23 µg/L has been established for one North American freshwater fish species (the Sheepshead minnow, *Cyprinodon variegatus*).

Information specifically related to carbofuran in water supplies for irrigation or livestock water could not be found. Ontario has a 0.1 mg/L water quality objective for the general category of carbamate and organophosphorus insecticides in livestock watering supplies.

Canadian drinking water quality guidelines for carbofuran do not exist at this time. The U.S. EPA Office of Drinking Water has recently recommended a guideline of 0.036 mg/L for carbofuran.

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3. INTERSPECIES VARIABILITY IN RESPONSE TO CHOLINESTERASE INHIBITORS AND QSAR (A. Baril, Ottawa, Ontario)

Introduction:

The variability in toxic response between several, often closely related species, makes the process of hazard evaluation exceedingly difficult since many different species could be expected to be exposed during any given pesticide application.

One of the major and growing concerns of the Canadian Wildlife Service is the acute toxic impact of organophosphate and carbamate insecticides (two classes of chemicals that inhibit cholinesterase) on wildlife.

A literature review was, therefore contracted out on interspecies variability with respect to these two classes of insecticides and inquired specifically whether any characteristics of the pesticide molecules themselves Quantitative Structure Activity Relationships (QSAR) could be of assistance in elucidating interspecies differences.

Methodology:

A thorough literature search of avian and mammalian toxicology, cholinesterase inhibitors and QSAR predictors was undertaken.

Results and Discussion:

A report was produced which addressed the following questions:

1. What were previous attempts to compare lethal (oral, dermal, and inhalation LD_{50} or LC_{50}) and sublethal toxicity endpoints of organophosphates and carbamates between different vertebrate species?

2. What are the sources of variability among species? and

3. Are structure-activity relationships applicable to the prediction of acute toxicity invertebrates?

A data-base format was set up in order to compile the relevant toxicological and physico-chemical data from company submissions for future analysis by the evaluation group.

A number of avenues for observing interspecies comparisons were identified in the report. Unfortunately, most required the acquisition of base data such as various physiological measurements on the species of concern.

Also, while structure-activity relationships have been useful for elucidating the cholinesterase-inhibiting potential of homologous series of molecules, successful predictions of the activity of randomly selected chemicals is beyond our present capabilities.

Finally, there has not been any demonstrated link between any species attributes (whether avian or mammalian) and structure-activity characteristics of organophosphates or carbamates.

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4. SENSITIVE ACE MICROASSAY AND ITS APPLICATION TO QUANTIFICATION OF EXPOSURE OF WILDLIFE TO NON-PERSISTENT PESTICIDES

(D.B. Peakall, S. Kennedy and S. Trudeau, Canadian Wildlife Service)

Introduction:

Inhibition of acetylcholinesterase (AChE) is the standard technique for assessing exposure to organophosphate and carbamate pesticides. Nevertheless, there is a need for improving the reproducibility and sensitivity of the technique and to improve and standardize the methods of collecting samples for analysis under field conditions. In addition to methods development work, several studies, both field and laboratory, were undertaken.

Methodology:

The basic method used was a modified Ellman's technique. This technique was set up successfully for both brain and plasma and could be modified for use with an autoanalyser. The automation is largely completed, although some final validation is needed. When completed, automation would permit about 120 determinations of plasma to be carried out per day. The Augustinsson method was tried but could not be successfully modified to avian blood. A chemical reactivation technique, using 2-PAM, to separate inhibition resulting from organophosphates and carbamates was set up for operational use.

Results and Discussion:

a) Collection and preservation of plasma samples. It was determined that plasma samples could be thawed, analysed, refrozen, rethawed and still give reproducible results as long as they were kept on ice during manipulations.

Heparinized capillary tubes was the method of choice for collecting blood from the bird's wing vein. The plasma was clear after centrifuging and could be frozen in the capillary. Vacutainers, while giving larger volumes, were less reproducible as the plasma was sometimes cloudy (which interfered with the AChE determination) and there were problems with the vein collapsing.

The direct heart puncture technique worked well and was used when the bird was be to sacrificed for determination of brain AChE.

b) Preparation and preservation of brain homogenates. A standardized homogenizing procedure was developed. The following comparisons were made;

1. fresh versus frozen homogenates,
2. centrifuged versus non-centrifuged homogenates, and
3. homogenates prepared with detergent versus those prepared with buffer.

The following results were obtained:

1. It was found that frozen homogenates gave inconsistent results. If freezing is necessary, then the brain should be frozen before homogenizing.
2. No differences were found between centrifuged and non-centrifuged homogenates.
3. No differences were found between homogenates prepared with buffer and those prepared with detergent.

c) Filter paper technique. This approach was assessed for use in the field. Pooled blood from control and exposed quail were applied to two different filter papers (Millipore and Whatman). The blood absorbed better and dried faster on the Millipore discs. However, for both papers problems were encountered in the extraction procedure. The solutions obtained, both with water and Triton X-100, could not be analysed due to the formation of a jelly. Further studies are needed.

d) Field studies.

1. Degree of inhibition of plasma cholinesterase was determined on the plasma of 44 specimens of burrowing owl. Twenty-two samples were controls: nine samples from birds one day after exposure to Sevin; ten samples four days after exposure to Furadan and Sevin; two samples four days after exposure to Furadan; and two samples after exposure to Lorsban. No differences in the ChE activity were found in owls exposed to spraying events within 400 metres of the nest burrow.

2. Activity of plasma cholinesterase was determined in 35 control and 26 Brewer's blackbirds exposed to carbofuran. No difference in the activity level was found between the two groups.

3. The activity of cholinesterase in the brain was determined for two Peregrine Falcon specimens. No control data is available, but the ChE levels were in the same range as control matter from other species.

4. The ChE activity in the brain of five geese found dead and two controls were compared. The levels in the five geese was about 1/3 of the control values. Reactivation using 2-PAM restored these values to normal levels, suggesting that the inhibition was caused by an organophosphate. Diazinon had been applied to the lawn where the dead geese were found.

Automated procedures: The determination of plasma and brain cholinesterase including reactivation techniques were put into place. It was found that plasma homogenates could be thawed and refrozen without causing problems. However brain homogenates could not be successfully frozen. Considerable difficulties were found with the filter paper technique to preserve avian blood and further work will be needed before this technique can be applied to field samples. The degree of inhibition of AChE was determined for a number of field studies.

e) Reports available

Trudeau, S. "Plasma Cholinesterase Activity Determination. 1986 Burrowing Owls", Internal NWRC Report (April, 1987).

Trudeau, S. "Plasma Cholinesterase Activity Determination. 1986 Brewers Blackbird Study", Internal NWRC Report (April, 1987).

Trudeau, S. "Brain Cholinesterase Activity Determination. Peregrine Falcons 34751, 35988", Internal NWRC Report (April, 1987).

Trudeau, S. "ChE Activity Determination. Goose brains." Internal NWRC Report (March, 1987).

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5. SUBLETHAL PORPHYRIC EFFECTS OF PESTICIDES ON BIRDS

(David B. Peakall and S. Kennedy, National Wildlife Research Centre, Canadian Wildlife Service)

Introduction:

The objectives of this study were: to determine the potential of liver porphyrin patterns as indicators of sublethal toxicity of organophosphate insecticides to birds; and to compare the results obtained by exposure of intact birds to those obtained in a chicken embryo liver cell culture to evaluate this in vitro system. Successful validation of the in vitro approach could drastically reduce the number of animals needed to test pesticides.

Methodology:

Japanese Quail (*Coturnix coturnix japonica*) were dosed for six weeks with three organophosphate insecticides (diazinon at 10, 25, 50 and 100 ppm; chlopyrifos at 4, 10, 20 and 40 ppm, and fenitrothion at 75, 100, 150 and 250 ppm). Quail were also dosed with hexachlorobenzene at 5 and 50 ppm as a positive control. Porphyrin patterns in liver were determined by high pressure liquid chromatography (Kennedy et al., 1986). Cholinesterase activity was measured in plasma and brain.

Results and Discussion:

Inhibition of cholinesterase activity was observed in the diazinon-treated birds and mortality was observed in the highest dose group. However, there was a lack of dose response between dosage of diazinon and degree of cholinesterase inhibition, and further a lack of correlation between the degree of cholinesterase inhibition in the brain and plasma. Porphyrin concentrations in the liver were not affected by diazinon.

Chlorpyrifos caused a dose-dependent inhibition of plasma cholinesterase over most of the range studied, but did not cause a decrease of brain cholinesterase. The highest dose of fenitrothion used (250 ppm) caused marked lethargy and some mortality. Those birds on the 150 ppm diet showed some lethargy, other groups appeared normal. Both plasma and brain cholinesterase were inhibited, but there was a lack of correlation between the two measurements and no clear dose response. Neither chlorpyrifos nor fenitrothion caused porphyria, although the latter compound caused a modest increase in the levels of coproporphyrin.

Hexachlorobenzene caused a marked porphyric response. Coproporphyrin was markedly and protoporphyrin mildly elevated at both doses. The highly carboxylated porphyrins showed moderate elevation at the low dose and a more marked increase at the high dosage. Hexachlorobenzene caused an increase in plasma cholinesterase activity. The effect was not dose dependent, and no effect upon brain cholinesterase was observed.

Cell culture experiments, using the livers from 17-day old chicken embryos, were carried out to compare the finding with the in vivo studies in order to determine the validity of the in vitro approach. The polychlorinated biphenyl, Aroclor 1254, was used as a positive control. Chlorpyrifos was found to be strongly porphyrogenic and produced a similar porphyrin pattern to Arochlor 1254. Fenitrothion was also porphyrogenic, but the pattern of the response was different, with coproporphyrin rather than the highly carboxylated porphyrins showing the most marked increases. Cell culture results on diazinon are not available.

The sensitivity of plasma cholinesterase to organophosphates and the lack of correlation of this response to brain cholinesterase activity is of concern. There is also a lack of correlation of inhibition of cholinesterase with other parameters such as behavioural changes. These differences are of importance since inhibition of cholinesterases in birds is widely used to monitor exposure to organophosphate insecticides. Porphyrogenic responses were found to be markedly different in vitro to those found in vivo.

A final report on contract KN107-6-4122 has been submitted by ANATOX and is available. Future studies will be needed to explain the lack of dose response of cholinesterase inhibition and the differences between the in vitro and in vitro results.

References:

Kennedy, S. et al., Anal. Biochem., 157, 1-7 (1986)

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6. PESTICIDE USAGE IN LATIN AMERICA (Dr. D.B. Peakall National Wildlife Research Centre, Canadian Wildlife Service)

Introduction:

The objectives of this study were to produce an overview of the current pesticide situation in Latin America including projections of future use patterns. Since many species of birds migrate from Canada into Latin America in the winter the exposure of Canadian breeding populations in Latin America is a significant amount of the total exposure of these populations to pesticides.

The specific objectives of this project were:

1. to compile the import and manufacturing data of individual pesticides in Latin America, on a country-by-country basis;
2. to compile the usage patterns of pesticides within the individual countries; and
3. to prepare generalized land use maps, with emphasis on agriculture and forestry.

Methodology:

The work was carried out through a contract to Dr. Philogene at the University of Ottawa. The information was obtained by literature searches and by contacting national and international organizations involved in the pesticide field. A total of 58 documents were obtained and used in the compilation of the final report.

Results and Discussion:

A wide variety of insecticides, herbicides and fungicides are used in Latin America. Over 90% of the pesticides are used in Argentina, Brazil, Columbia and Mexico and these include many pesticides banned in the exporting countries. Nevertheless, there is a general trend away from the use of organochlorine insecticides and some have been banned in some countries. Little increase of pesticide usage is projected for the next ten years, but the movement away from organochlorines will cause considerable increases in expenditure. Herbicide use is forecast to increase substantially in the next ten years, whereas only a slight increase of the use of fungicides is projected.

The report gives a useful, but broad, overview of the current patterns and likely future trends in pesticide usage in Latin America. The project has been completed and a final report is available.

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PESTICIDES PROGRAM IN THE ATLANTIC REGION

(Nova Scotia, New Brunswick, Prince Edward Island, Newfoundland)

1. THE INFLUENCE OF pH ON THE ACUTE LETHALITY OF FENITROTHION, 2,4-D AND AMINOCARB, AND SOME pH-ALTERED SUBLETHAL EFFECTS OF AMINOCARB ON RAINBOW TROUT

(K.G. Doe, W.R. Ernst, W.R. Parker, G.R. Julien and P.A. Hennigar, Contaminants and Assessments Branch, C&P, Atlantic Region)

Introduction:

The objective of the study was to determine if a change in water quality (pH) altered the toxic effects of several pesticides.

Methodology:

Aminocarb, fenitrothion and 2,4-D were tested in static, 96-h acute lethal toxicity bioassays, using fingerling rainbow trout (*Salmo gairdneri*) at pH 4.6, 5.6, 6.9 and 8.5.

A subsequent test was performed to determine the effect of two exposure pH's on brain acetylcholinesterase activity and whole body pesticide residue of rainbow trout fingerlings exposed to aminocarb. Fish were exposed to aminocarb solutions which had a pH of 4.5 or 8.5.

Results and Discussion:

The toxicity of aminocarb, a base, increased notably with increasing pH. Conversely, the toxicity of the acid pesticide 2,4-D increased with decreasing pH. The toxicity of the neutral pesticide, fenitrothion, did not change significantly with changing pH.

Brain acetylcholinesterase activity was inversely proportional to the aminocarb content of whole fish. In fish exposed to aminocarb at pH 4.5, brain acetylcholinesterase was maximally depressed at six hours, after which it recovered to within the range of control values and remained there until the end of the test. Aminocarb concentrations rose to a maximum of 9.1 µg/g within six hours at this pH, after which they declined to a level of 1 µg/g at 25 hours and remained constant for the 96-h duration of exposure. In the fish exposed at pH 8.5, however, brain acetylcholinesterase values dropped below the control range of values by one hour and remained below control values until all fish died by 72 hours. A maximum aminocarb concentration of 12.0 µg/g was reached within one hour at this pH, and remained elevated until the fish died at 72 hours. Several explanations for the observed results are presented. Presumably pesticide elimination or metabolic rates allowed the fish to cope with the exposure regime at the lower pH, but not at the higher pH.

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2. MEASUREMENT OF OFF-TARGET MOVEMENT OF AERIAL APPLICATIONS OF AGRICULTURAL PYRETHROID PESTICIDES AND THEIR IMPACT ON AQUATIC FAUNA

(Part 1 - Aerial Drift - Dr. Charles Wiesner, Mr. Chris Riley, Research and Productivity Council of New Brunswick; Part 2 - Pesticide Deposit and - Biotic Impact - W. Ernst)

Introduction:

The agricultural use of synthetic pyrethroid pesticides, such as deltamethrin, fenvalerate, and permethrin, is of concern to environmental agencies, due to their effects on non-target organisms, particularly aquatic fauna. A condition of the temporary registration of such products in Canada is that when they are applied by air, a 100-metre set-back from watercourses must be observed.

The objectives of the study were to:

1). measure the drift and deposit of aerially applied agricultural pyrethroid pesticide sprays, under three separate conditions, up to 100 metres downwind; and

2). measure the deposit and biological impacts on two ponds, one directly oversprayed and one which was protected by a 100-metre spray buffer zone.

Methodology:

The drift and deposit of deltamethrin sprays up to 100 metres downwind of the target site were measured under three different meteorological conditions. The effectiveness of 100-metre set-backs in preventing unacceptable deposit was also measured by studying biological impacts, on pond systems.

Results and Discussion:

The deposits, measured on stainless steel plates, were reduced by approximately one order of magnitude, compared with the edge of field deposit, within 100 metres downwind. Spray flux, measured by rotorod sampling, reflected the trends in off-target deposit. The two ponds which were studied, one directly oversprayed and one protected by a 100-metre set-back, demonstrated very different responses after three separate treatments to each. Protecting one of the ponds with the set-back reduced mean measured surface water concentrations and mean measured deposit by 1/145 and 1/450 (respectively) when compared with the oversprayed situation. Likewise no effects on caged fish, caged aquatic invertebrates and invertebrates on artificial substrates could be measured in the set-back pond while major biotic impacts could be measured in the oversprayed pond. The utility of 100-metre set-backs for these types of application was established.

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3. MEASUREMENT OF THE ENVIRONMENTAL EFFECTS ASSOCIATED WITH FORESTRY USE OF ROUNDUP

(W. Freedman, R. Morash, K. Fletcher, Biology Dept., Dalhousie University; R. McCurdy, Environmental Chemistry Labs, Victoria General Hospital, Halifax; W. Ernst, G. Julien and P. Hennigar, EP, Dartmouth)

Introduction:

Herbicides are becoming an increasingly popular tool in forestry for the control of competitive vegetation. Roundup, which contains the active ingredient glyphosate, is now the herbicide used almost exclusively for this purpose. The published data base for the environmental effects of glyphosate is much smaller than that of the chlorophenoxy herbicides which were previously popular. Accordingly, a number of studies were undertaken to determine the environmental effects of Roundup use in Nova Scotia and, in some instances, to compare these effects with those documented for 2,4-D and 2,4,5-T.

The objective of this project was to document the environmental effects of operational forestry use of Roundup herbicide. The study was done in four parts:

a) measurement of spray deposit within, and immediately outside of spray blocks;
b) persistence of deposited glyphosate in foliage and forest litter;
c) effects of herbicide treatments on litter decomposition; and
d) effects of deposited glyphosate on stream periphyton.

Methodology:

a) Deposit of ground and aerially applied herbicide was measured on flat plates using rhodamine dye as a tracer. Applications were at normal operational dosage rates and twice normal rates.
b) The persistence of glyphosate on foliage and litter from sprayed plots was also measured by GC techniques. Foliage analysed was red maple (*Acer rubrum*), balsam fir (*Abies balsamea*), raspberry (*Rubus* spp.) and grasses (*Poaceae* and *Cyperaceae*).
c) The rate of decomposition of litter, both in the field and in the laboratory after treatment with herbicide was also explored. Substrates were: collected forest floor material (litter, duff and humus), fresh red maple or white spruce (*Picea glauca*). Samples of substrate were dosed in the laboratory or placed in field plots which were subsequently dosed with herbicide.
d) The final study determined stream residue concentrations following direct oversprays at operational dosage rates and if such concentrations affect stream periphyton abundance. Artificial substrates were placed in a stream above and below the influence of spray, sampled at various times after spray and analysed for chlorophyll a, phaeophytin, biomass and ATP content.

Results and Discussion:

a) The results of the first study indicated that deposit was highly variable; however, ground applications provided the highest rate of deposit inside the target with no measurable off-site deposits. Aerial sprays resulted in measurable deposit up to 95 metres off target.
b) The results of the second study indicated that highest concentrations of glyphosate were detected the day after spraying in raspberry and grasses (13 mg/g and 12 µg/g dry weight) respectively. Red maple, forest litter and balsam fir had concentrations of 5.1 mg/g, 2.6 mg/g and 0.09 µg/g dry weight, respectively, one day after spray. Residues in all substrates, with the exception of forest litter, declined rapidly up to 58 days post-spray. Forest litter residues demonstrated an overall decline; however, the rate was less rapid than in foliage.
c) The results in this study showed that the amount of decomposition decreased with increasing amounts of dosages of 2,4-D, 2,4,5-T, a 50:50 mixture of 2,4-D and 2,4,5-T and glyphosate; however, these effects were only significant at concentrations greater than 1000 ppm. Thus, only at these very high concentrations were any of the herbicides toxic enough to significantly reduce microbial activity.
d) This study showed that stream residues were highly variable immediately after spray with the highest concentration (39 µg/L) being measured 30 hours post spray. Periphyton abundance data was variable; however, no large changes were noted up to 37 days after spraying.

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4. ASSESSMENT OF PRINCE EDWARD ISLAND GROUNDWATERS FOR THE PESTICIDE ALDICARB

(W. Ernst/R. Matheson, Contaminants and Assessments Branch, C&P, Atlantic Region)

Introduction:

In a 1982 survey, aldicarb was identified as one of the most intensively used pesticides in Prince Edward Island. In addition, Prince Edward Island soils exhibit characteristics similar to areas in the United States where aldicarb residues have been detected in groundwaters. As a consequence of these two factors, an eighteen-month sampling program was initiated to determine the distribution and concentration of aldicarb in Prince Edward Island groundwaters.

The objective of this project was to determine the extent and magnitude of aldicarb contamination of groundwaters in P.E.I. which underlay agricultural areas where the pesticide is used.

Results and Discussion:

Depending on sampling time, aldicarb residues of 1 ppb or greater were detected in 5 to 27% of tested wells. For the most part, detectable levels ranged from 1.0 to 3.0 ppb, with 5.4 ppb the maximum reported value. The incidence of detection was directly related to the distance of a sampled well from a treated field, the time between pesticide application and sampling, the history of aldicarb use in the treatment area and well construction.

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5. PESTICIDE MIGRATION AND FATE IN GROUNDWATER (R.E. Jackson, K.S. Novakowski, S. Lesage, M.W. Priddle, P. Lapcevic and G. Bobba)

Introduction:

Until the extremely toxic carbamate pesticide, aldicarb, was detected in the groundwaters of Long Island, NY in 1979, it was widely believed that pesticides did not pose a threat to groundwater. It is now accepted, largely because of this experience, that any soluble, persistent pesticide when applied to a crop on sandy soils may be leached to the water table.

In Canada, several pesticides have been identified in rural wells (e.g., traces of alachlor, atrazine and metalochlor in southern Ontario and 1,2-dichloropropane in British Columbia). However, by far the most serious situations have arisen because of aldicarb contamination of wells in the potato-growing areas of Ontario, Quebec, New Brunswick and Prince Edward Island (P.E.I.), sometimes at concentrations in excess of the interim Canadian drinking water guideline of 9 ppb (Health and Welfare Canada, 1986).

In the Maritimes, aldicarb has caused the greatest concern for the protection of groundwater supplies, which provide 50% of Nova Scotia's water supply, 60% of New Brunswick's and 100% of P.E.I.'s. A recent Environment Canada report on the potential for pesticide contamination of groundwater in the Atlantic provinces identified aldicarb, carbofuran, dinoseb and atrazine as the highest priority pesticides and called for "more data on the environmental fate and behaviour of pesticides in soil and groundwater".

The objective of this study was to assess the migration and fate of aldicarb/Temik in groundwaters beneath potato fields in Prince Edward Island.

Methodology:

In 1985 Environment Canada established two field sites in P.E.I. to determine the migration and fate of aldicarb applied to potatoes grown there. A third site was added in 1986 and the first two had additional instrumentation installed so that there is now a total of 50 piezometers of monitoring wells distributed over the three sites. These small-diameter wells were completed and screened in the sandstone aquifer which underlies the whole of P.E.I. and forms the sole source water supply. Chemical and hydraulic testing of the wells has been undertaken by the National Water Research Institute (NWRI) of Environment Canada based at the Canada Centre for Inland Waters in Burlington, Ontario. Groundwaters were sampled and analysed for dissolved constituents such as pH, dissolved oxygen and ammonia, nitrate and aldicarb. Data from three sites have enabled NWRI to identify processes that are site-specific as well as generic.

Results and Discussion:

Generally, it is known that groundwater environments of acid pH and average temperature (i.e., 10°C) result in the persistence of aldicarb. The very conditions that inhibit aldicarb degradation to less toxic products are found in the groundwaters beneath the Augustine Cove field site. Aldicarb is applied at seeding in the spring at which time soil waters exhibit the relatively low temperature and pH of the recent snowmelt. Because this is a period of high recharge, aldicarb degradation is inhibited and aldicarb infiltration is promoted. In groundwater, where the temperatures are relatively constant at 8 to 10°C, pH becomes the controlling factor in promoting aldicarb degradation, which is enhanced in alkaline groundwaters. The sandstones of P.E.I. are relatively low in natural mineral carbonates. Consequently this process is limited, especially in areas where the recharge is predominately through fractures in the sandstone and where the water table is shallow so that the contact time in the unsaturated zone is short. Furthermore, the application of ammonium and area fertilizers inhibits the degradation process, as there is sufficient dissolved oxygen in the groundwater for the oxidation of the ammonium to produce a pronounced drop in pH.

None of these conditions, however, exist at the Mill Valley site. The water table at Mill Valley is from 3 to 10 metres deep and the groundwater has a pH range of 7.5 to 8.0. Consequently, the concentration of total aldicarb in groundwater has not been measured in excess of 1.05 ppb, except at a spring draining a shallow perched water table (< 5 ppb). The third site, at New Annan which was instrumented through funds provided by Environment Canada's "Pestfund", appears similar to the Mill Valley site rather than the Augustine Cove site.

Generally, it would seem that the best time to apply aldicarb or Temik to potato fields is after plant emergence in June. Due to the higher soil temperatures of June and the likelihood that ammonium concentrations would by then have decreased somewhat, it is probable that aldicarb degradation will proceed more rapidly, consequently it is less likely that aldicarb will contaminate nearby wells.

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6. PERSISTENCE AND FATE OF DELTAMETHRIN SPRAYED ON A POND AND STREAM IN PRINCE EDWARD ISLAND (R.J. Maguire and J.H. Carey)

Introduction:

The photostable pyrethroids, of which deltamethrin is one, are a relatively new class of pesticides which are notable for their high toxicity to insects and low mammalian toxicity. They have potential for large-scale use in agriculture and forestry. Pyrethroids are fairly toxic to aquatic insects and, indirectly, to organisms which feed upon such insects. For this reason, pyrethroid use is normally restricted to certain areas removed from streams or ponds. As part of a joint NWRI-EPS Atlantic Region-WQB Atlantic Region study on the effects of deltamethrin on aquatic biota, NWRI personnel examined the persistence and fate of deltamethrin in a pond and stream after a direct overspray.

The objective of this study was to contribute to an assessment of the hazard posed to aquatic organisms by the aerial spraying of deltamethrin on crops adjacent to bodies of water.

Methodology:

After the spraying of deltamethrin on a pond and a stream adjacent to a potato field in Prince Edward Island in July 1986, samples of subsurface water, surface microlayer, suspended solids, sediment and benthic invertebrates were collected. These samples are analyzed for deltamethrin and four of its likely degradation products.

Results and Discussion:

Results to date indicate that deltamethrin disappears from the surface microlayer very quickly, with a half-life of about 45 minutes. In both pond and stream small amount of metabolites were found; deltamethrin was not found in the sediments. In addition to completing the analyses, the sunlight photochemical degradation of deltamethrin on soil surfaces, and the relative importance of volatilization of deltamethrin from the surface microlayer and from the subsurface of natural waters are being investigated.

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BTS
ETU

7. RESIDUES OF PULP MILL SLIMICIDES IN THE VICINITY OF WOOD PROCESSING PLANTS (Wellington Environmental Consultants, Ontario, and Research and Productivity Council of N.B.)

Introduction:

The objective of the study was to determine the extent of environmental contamination by residues of parent compounds or metabolite of two of the most extensively used pulp mill slimicide products in the region - bis-trichloromethyl sulphone (BTS) and ethylene thiourea (ETU).

Results and Discussion:

Slimicide products are being used in the regional pulp and paper industry in substantial quantities, as indicated by a recent EPS inventory which found that approximately 17 000 kg of active ingredients are used annually by regional wood processing plants. Dithiocarbamate compounds, whose major metabolite is ethylene thiourea comprise over 50% of the slimicide active ingredient in use. Other extensively used products contain the bis-trichloromethyl sulphones. At each of two plants which use these products, water and sediment sampled were collected at various distances from outfalls up to a distance of two kilometres from the plants. No confirmed BTS residues were found in any samples taken from the vicinity of the plant using that product. ETU was detected in approximately 10% of the sediment samples and 25% of the water samples obtained from the plant using that product. Detectable concentrations of ETU in sediments ranged from 5 to 18 µg/kg while detectable water concentrations were all near the analytical detection limit of 5 µg/L. The concentrations of ETU detected do not constitute an environmental threat in themselves but may act in concert with other pollutants to degrade environmental quality.

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8. PESTICIDE USE INVENTORY FOR THE ATLANTIC PROVINCES (Seatech Investigation Services Ltd., Halifax)

Introduction:

Accurate pesticide use patterns are integral to the development of appropriate re-evaluation programs for registered pesticides. Usage data is imperative if priorities are to be properly identified and resources targetted in the most effective manner. In addition, the way in which pesticides are stored and handled can alter probability of their accidental release to the environment.

The objectives of this project were to:

a) identify and provide quantitative information on pesticides being used in the region in 1986;
b) determine local application rates and regimes;
c) flag those materials being used most extensively and intensively; and
d) determine the storage and handling capabilities of regional vendors.

Methodology:

Information was obtained from pesticide retailers in Nova Scotia and Prince Edward Island by means of a mailed questionnaire that was picked up in person. Where necessary, an interview was conducted. Results of this survey were compared with results of a similar survey conducted in 1982.

Results and Discussion:

Very similar amounts of pesticide active ingredient were sold in Nova Scotia and P.E.I. being approximately 158 000 and 152 000 respectively. This represented a slight increase over 1982 sales. Pesticide handling practices were judged to be generally good in both provinces however improvements in handler training and the development of better spill containment and emergency response plans were indicated.

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9. ENZYME IMMUNOASSAY AS A PESTICIDE RESIDUE MONITORING TOOL (Dr. C. Wiesner, Research and Productivity Council of N.B.)

Introduction:

A current limitation to the scope of many pesticide investigations is the cost and time factors associated with pesticide residue analysis by conventional gas chromatographic (GC) or high pressure liquid chromatographic (HPLC) techniques. Recently, enzyme immunoassay techniques have been developed by which concentrations of certain pesticides may be determined in environmental samples. This study compared available immunoassay analytical systems (EMIT) with conventional gas chromatographic techniques for detecting residues of aldicarb, aldicarb sulphone and aldicarb sulphoxide, in water samples.

The objective of this study was to assess the usefulness of available immunoassay analytical systems in providing a fast, simple and cheap procedure for the field analysis of pesticides, using aldicarb as an example. This was to be accomplished by:

a) determining detection limits, accuracy, and reproducibility of aldicarb analysis in water by enzyme immunoassay at the 100 to 500 ppb level versus state-of-the-art gas chromatographic analysis; and

b) developing simple sample concentration techniques in the range 10X to 1000X for aldicarb and its metabolites in order to extend detection limits to the 0.1 to 10 ppb range.

Methodology:

The concentrating effectiveness of a resin (LC-18 octadecyldimethyl silyl) column was tested by passing aldicarb fortified water (200 mL) through the column and subsequently extracting the columns with a solvent (methanol - 2 mL) suitable for the immunoassay.

Results and Discussion:

Recoveries from this technique were essentially quantitative resulting in a 100-fold concentration of the sample. Aldicarb sulphone and aldicarb sulphoxide yielded poorer and less reproducible recoveries (26 to 42% and 17 to 30%). The immunoassay analytical system provided a detection limit of about 200 to 400 ppb for aldicarb in the methanol concentrates (2 to 4 ppb in water); however, reproducibility in this range was poor with coefficients of variation of about 44%. At concentrations of 10 ppm, in extracts, reproducibility was somewhat improved (coefficients of variation were 15% and 32% after concentration). The cross-reactivity between aldicarb and the sulphoxide metabolite was also determined. This aspect was tested near the limit of detection and the results were somewhat equivocal, however, the mean aldicarb equivalent recovery rises from 117% at 0 ppb sulphoxide to 194% at 10 ppb sulphoxide. At higher concentrations it would seem that the accuracy of the immunoassay is comparable to the GC methods.

EMIT is a registered trademark of Syva Corp., Palo, Alto, Ca.

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